STUDIES ON THE RAMAN EFFECT OF ORGANIC SUBSTANCES. VII. RAMAN EFFECT OF FURANE DERIVATIVES.

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Received September 3rd, 1936. Published November 28th, 1936.

Introduction. In one of the previous papers[1], the Raman spectra of α-mono-derivatives of furane were reported. Nearly at the same time, some of the furane derivatives were also studied by Bonino and Ansidei[2] and by Médard[3]. In the present investigation the Raman spectra of some α-mono-derivatives, α, α'-di-derivatives and α, β-di-derivatives, which have not been reported hitherto, have been studied in order to confirm the characteristic frequencies attributable to the furane ring and to study the constitutive influences exerted upon them. The more complete investigation will be reported after studying the other poly-substitution products of furane, which are now in the course of experiments.

Experimental. The substances used were synthesized by the following processes. α-Furfuryl methyl ether (I) (b. p. 134–136°) and α-furfuryl ethyl ether (II) (b. p. 148–150°) were prepared by Wissell-Tollens' method[4], that is, by warming the mixtures of α-furfuryl alcohol, F–CH_2OH,[5] and the corresponding alkyl iodides with potassium hydroxide. The ethers obtained were dried over calcium chloride and then fractionated over metallic sodium.

α-Furfuryl-acetone (III) (b. p. 101–102°/21 mm.) was obtained by reducing furfurylidene-acetone, F–CH : CH·CO·CH_3,[5] with 2.5% sodium amalgam in acetic acid solution, according to Harries and Kaiser[6].

α-Furyl-ethylene (IV) (b. p. 99°) was obtained by the decarboxylation of α-furfuracrylic acid, F–CH : CH·COOH[5], at about 260°C. The substance obtained was washed with aqueons sodium carbonate and dried over anhydrous sodium sulphate[7].

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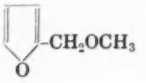
(1) This Bulletin, **9** (1934), 327.
(2) G. B. Bonino and R. Manzoni-Ansidei, *Z. physik. Chem.*, B, **25** (1934), 327.
(3) L. Médard, *Bull. soc. chim.*, (5), **1** (1934), 934.
(4) L. von Wissell and V. Tollens, *Ann.*, **272** (1893), 297.
(5) F denotes α-furyl-group – in this paper.
(6) C. Harries and Friedrich Kaiser, *Ber.*, **32** (1893), 1320.
(7) C. Liebermann, *Ber.*, **27** (1894), 287.

α-Furyl cyanide (V) (b. p. 146–147°) was prepared by treating α-furfuraldoxime, F-CH : NOH, with acetic anhydride according to Pinner[8].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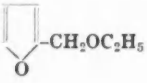
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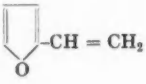
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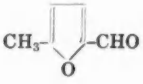
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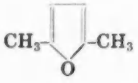
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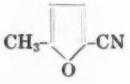
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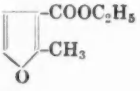
IX

2-Methyl-furfural-(5)[9] (VI) (b. p. 83–85°/15 mm.) was prepared by reducing a mixture of hydrochloric acid (sp. gr. 1.173) and ordinary sugar with stannous chloride.

2,5-Dimethyl-furane (VII) (b. p. 93°) was prepared by dropping small pieces of potassium hydroxide into a mixture of 2-methyl furfural-(5), hydrazine hydrate and methyl alcohol under sufficient cooling (Wolff-Kischner's method)[10]. The substance obtained was washed with a saturated aqueous solution of calcium chloride and sodium bisulphite. It was, then, dehydrated over calcium chloride and redistilled over metallic sodium under normal pressure.

2-Methyl-furyl cyanide-(5)[11] (VIII) (b. p. 65°/10 mm.) was prepared from α-furfuryl chloride and aqueous potassium cyanide. α-Furfuryl chloride[12] was obtained by treating α-furfuryl alcohol with thionyl chloride and pyridine in absolute ether.

Ethyl 2-methyl-furoate-(3)[13] (IX) (b. p. 100–101°/25 mm.) was prepared by treating a mixture of 1,2-dichlorether (b. p. 140–145°) and ethyl acetoacetate with aqueous sodium hydroxide.

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(8) A. Pinner, *Ber.*, **25** (1892), 1415.
(9) "Organic Syntheses", Vol. XIV, p. 62 (1934).
(10) This Bulletin, **9** (1934), 327.
(11) T. Reichstein, *Ber.*, **63** (1930), 749.
(12) W. R. Kirner, *J. Am. Chem. Soc.*, **50** (1928), 1955.
(13) H. Gilman and R. Robert, *Rec. trav. chim.*, **51** (1932), 408.

About 3–10 c.c. of each sample was used. The Raman spectra were taken by means of a spectrograph with three prisms[1]. The results are shown in Table 1. The numbers of the Raman lines(n), the number of the plates, and the conditions under which the spectra were taken, are summarized in Table 2. 2,5-Dimethyl-furane has been studied by Bonino and Manzoni-Ansidei[2]. Their results are in good agreement with those reported in the present paper. On account of the colouration, the Raman spectrum of 2-methyl-furfural-(5) (VI) could not be observed completely, except some of the intense lines, viz., $\Delta\nu$ 1355, 1375, 1521, 1590, 1675 and 3122 cm^{-1}. The all data and the photograph of this substance are omitted in this paper.

Table 1. The $\Delta\nu$ Values of the Raman Spectra of Furane Derivatives.

(1) α-Furfuryl methyl ether (I).

140 (3b, d); 166 (3); 383 (3bb, d); (433) (0)?; 466 (2); (604) (½); 627 (4d); 642 (3); (740) (1bb. d); (819) (1bb, d); 883 (5); 901 (4); 920 (4); 951 (5b, d); 1018 (4); 1077 (8); 1150 (5); 1224 (6d); (1291) (1); 1384 (8b); 1445 (3d); (1473) (½)?; 1501 (10); 1593 (6d); 2819 (5); 2841 (0); 2894 (½); 2938 (1); 2985 (½); 3116 (6b, d); 3141 (2).

(2) α-Furfuryl ethyl ether (II).

(167) (1b, d); 351 (2); (384) (0); 627 (2); (640) (0); (807) (0d)?; 840 (2); 887 (3); 923 (3); (971) (1d); 1018 (3d); 1078 (6d); 1150 (2); 1223 (5b, d); 1384 (6d); 1444 (3b, d); 1501 (10); 1594 (5d); 2930 (5); 2974 (4); 3115 (6b, d); 3145 (5).

(3) α-Furfuryl-acetone (III).

625 (0); 650 (½d); 732 (½)?; 748 (1); 807 (0)?; 876 (1d); 938 (1d); 1020 (½); 1041 (2b, d); 1083 (5); 1150 (5bb, d); (1209) (1d); 1250 (½); 1292 (½)?; 1388 (4d); 1412 (½); 1446 (1d); 1477 (2); 1509 (10); 1597 (6d); 1679 (2); 1721 (3); 2918 (3); 2974 (½); 3120 (4d); (3155) (4d).

(4) α-Furyl-ethylene (IV).

217 (6); (368) (½b, d); 481 (5); 655 (5); 716 (2d); (736) (½b, d); (811) (1d); 885 (3); 908 (1); 925 (4); 1002 (1); (1017) (½); 1027 (8); 1079 (4d); 1145 (3b, d); 1216 (5); 1255 (3); 1292 (8d); 1387 (8); 1491 (10); 1576 (4); 1642 (10); 3004 (½); 3125 (3); (3154).

(5) α-Furyl cyanide (V).

183 (8); (311) (½); 570 (8s); 591 (1s); 640 (5); 655 (4); 761 (1d); 837 (2d); 887 (6d); 928 (6); 938 4b); 1020 (7); 1072 (8); 1151 (8); 1232 (6); 1379 (10); (1456) (2); 1471 (10b); 1566 (6); 2233 (10); 3133 (5d); 3156 (3).

(6) 2,5-Dimethyl-furane (VII).

266 (2d); 290 (1d); 396 (0); (445) (½); 610 (5); 689 (1); 781 (0); 923 (½); 991 (2); 1018 (3); 1086 (2b, d); 1217 (5d); (1269) (1); 1351 (2); 1379 (2); 1452 (4d); 1503 (1); 1573 (8); 2926 (6d); 2956 (½d); 2975 (½); 3118 (3).

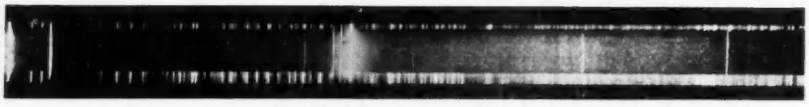
Table 1. (*Concluded*)

(7) 2-Methyl-furyl cyanide-(5) (VIII).

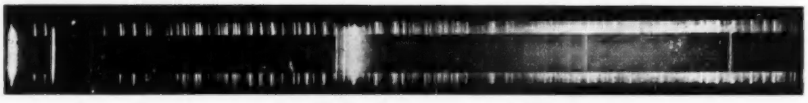
164 (4d); 260 (2d); 343 (½d); 386 (2d); 433 (½); 493 (½); 616 (1); 649 (3); 675 (0); 952 (½); 999 (1); 1028 (5); 1202 (4); 1223 (2); 1356 (3d); 1388 (2); 1449 (½); 1507 (2); 1523 (10); 1570 (0); 1600 (6); 2231 (8); 2932 (4); 2977 (½); 3120 (3d).

(8) Ethyl 2-methyl-furoate-(3) (IX).

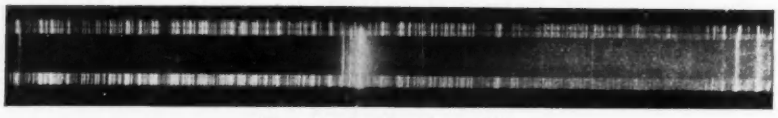
327 (1d); 359 (1d); 609 (2); 638 (3b); 684 (4b); 775 (2); 833 (1d); 869 (4d); 899 (6); 948 (2); 1013 (3d); 1041 (6); 1236 (2d); 1304 (6); 1345 (2); 1372 (2); 1396 (3); 1415 (3); 1453 (4b, d); 1522 (10); 1603 (6b, d); 1716 (6b, d); 2932 (8b, d); 2979 (3b, d); (3120) (4d); 3157 (½).



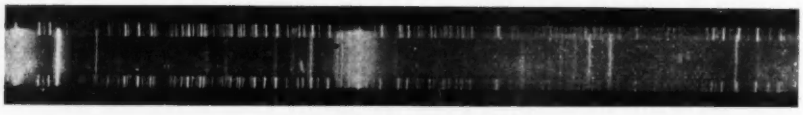
(1) α-Furfuryl methyl ether (I)



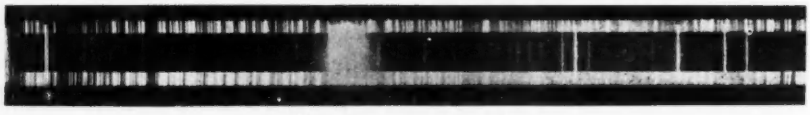
(2) α-Furfuryl ethyl ether (II)



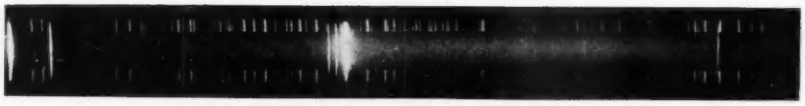
(3) α-Furfuryl-acetone (III)



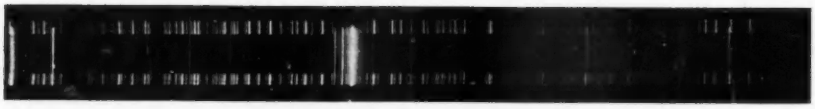
(4) α-Furyl-ethylene (IV)



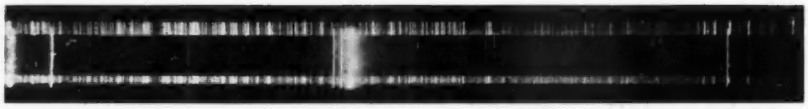
(5) α-Furyl cyanide (V)



(6) 2, 5-Dimethyl-furane (VII)



(7) 2-Methyl-furyl cyanide-(5) (VIII)



(8) Ethyl 2-methyl-furoate-(3) (IX)

Table 2.

Substance	n	No. of plates	Width of slit (10^{-2} mm.)	Temp. (°C.)	t (hours)
α-Furfuryl methyl ether (I)	56	210	70	23	8
		211	64	23	10
α-Furfuryl ethyl ether (II)	44	221	70	30	8
		222	64	30	10
α-Furfuryl-acetone (III)	29	257	75	25	8
α-Furyl ethylene (IV)	53	231	70	28	6
α-Furyl cyanide (V)	44	225	70	30	8
		226	64	30	10
		290	75	24	5
		291	70	25	14
2,5-Dimethyl-furane (VII)	36	328	70	26	6
		329	70	25	8
2-Methyl-furyl cyanide-(5) (VIII)	39	229	70	28	6
		230	70	28	8
Ethyl 2-methyl-furoate-(3) (IX)	38	247	70	26	6
		248	64	26	8
		256	64	25	8

Discussion. The Raman lines corresponding to ω_1 626, ω_2 885, ω_3 923, ω_4 1018, ω_5 1083, ω_6 1150, ω_7 1223, ω_8 1384, ω_9 1505, ω_{10} 1602, ω_{11} 3117, and ω_{12} 3150 cm.$^{-1}$ in α-furfuryl-acetone (III), α-furfuryl methyl ether (I), and α-furfuryl ethyl ether (II) are in good coincidence with those in α-methyl-furane, F–CH_3, α-furfuryl alcohol, F-CH_2·OH, and α-furfuryl acetate, F-CH_2·O·CO·CH_3, which have been reported in Part III[1] (See Table 3). As to the other α-furyl- and furoyl-compounds, such as α-furyl-ethylene, α-furyl cyanide and alkyl furoates, these characteristic frequencies are also nearly constant, excepting ω_9 and ω_{10} (Table 4). The frequency of ca. 960 cm.$^{-1}$ and those in the region of $\Delta\nu$ 810 and 740 cm.$^{-1}$ appear also in most of the α-mono-derivatives of furane.

It is remarkable that the intense lines at ω_2 885, ω_6 1150 and ω_{12} 3150 cm.$^{-1}$ in α-mono-derivatives, are not observed in the α, α'-di-derivatives of furane, such as 2,5-dimethyl-furane and 2-methyl-furyl cyanide-(5). The intense line corresponding to ω_5 1083 cm.$^{-1}$ in α-mono-derivatives disappears in 2-methy-furyl cyanide-(5) and appears weakly in 2,5-dimethyl-furane, while a new line corresponding to $\Delta\nu$ 1355 cm.$^{-1}$ is observed in the α, α'-di-derivatives.

It is of interest to note that, in the case of α-mono-derivatives of furane, two frequencies, ω_9 and ω_{10}, in the region between 1460 and 1600 cm.$^{-1}$ are slightly reduced by the constitutive influence of the unsaturated side chain attached to the furane ring. As shown below in Table 6, in passing from α-methyl-furane to α-furyl-ethylene and α-furyl cyanide, the corresponding frequenies, ω_9 and ω_{10}, are reduced about 20 in wave numbers.

The frequencies in question in other furane derivatives which have been observed hitherto, are summarized in Table 5. A glance at Table 5 will lead to the conclusion that, in α-furfuryl-compounds, F–CH_2–X, ω_9 and ω_{10} remain nearly constant, while in the furfurlidene-compounds, F-CH = CH–X, a slight decrease of ω_9 is found. The mean values of ω_9 and ω_{10} are taken as $\Delta\nu$ 1505 and 1600 cm.$^{-1}$ for furfuryl, and $\nu\Delta$ 1480 and 1575 cm.$^{-1}$ for furfurlidene- or furoyl-compounds, while the corresponding ones in furyl cyanide are $\Delta\nu$ 1471 and 1566 cm.$^{-1}$

Table 3. Raman Spectra of α-Furfuryl-compounds. (F:)

	F-CH_3	F-CH_2·CH_2·$COCH_3$	F-CH_2-OH	F-CH_2·O·CO·CH_3	F-CH_2·OCH_3	F-CH_2·OC_2H_5
	253 343		177 421	172 193 315 332	140 166 383 469	167 351 384
ω_1	626 654	625 650	603 626	621 659	604 627 642	627 640
	718	732 748	741	745		
	796 (855)	807	816	835	819	796
ω_2	888	876	888	886	883	885
ω_3	917 (976)	938	922 959	924 964	901 920 951	923
ω_4	1018	1018	1018	1022	1017	1018
ω_5	1084	1083	1083	1083	1077	1078
ω_6	1147	1150	1154	1153	1150	1150
ω_7	1215	1209	1228	1231	1224	1223
ω_8	(1376 1389	1390	(1374 1391	1389	1384	1394
Δ	1453	1446 1477	1477	1450	1473	1453
ω_9	1510	1509	1507	1505	1501	1501
ω_{10}	1605	1597	1602	1604	1593	1594
	2745 2888 2928 2955 3000	2811 2976	2940	2946	2821 2841 2939	2930 2974
ω_{11}	3119	3117	3117	3130	3116	3115
ω_{12}	3153	3160	3154	3156	3141	3145

Table 4. Raman Frequencies of α-Furoyl- and α-Furyl-compounds. (F:)

	F-CO·OCH$_3$	F-CO·Cl	F-CO·H	F-CH : CH$_2$	F-CH : CH·COOC$_2$H$_5$	F-C ⋮ N
	170 233 335 395 493	191 336 427 552	162 213 302 503	 217 368 481	 462	183 (311) 570
ω_1	602 618		598 630	 655	 635	591 640 655
	770 798	785 824	749 775	716 (736) (811)	768 794 862	761 837
ω_2	888	887	882	885	887	887
ω_3	911 922	950	928 945	908 925	939	928 938
ω_4	1019	1025	1019	1002 1017 1027	1021	1020
ω_5	1081	1084	1080	1079	1081	1072
ω_6	1122 1172	1163	1151 1159	1145	1160	1151
ω_7	1236	1232	1207 1223	1216	1212	1232
	1307	1254 ?	(1275) ?	1256 1292	1265 1283	
ω_8	1390	1388	1368 1393	1387	1392	1379
			1441			1456
ω_9	1478	1460	1463 1475	1491	1479	1471
ω_{10}	1572 1583	1560	1483 1568	1576	1575	1566
	1726	1744 1777	1668 1688	1642	1640 1704	 2233

Table 5. ω_9 and ω_{10} in α-Mono-derivatives of Furane. (F :)

F–H	1483[13]	
$F–CH_3$	1510	1605
$F–CH_2CH_2COCH_3$	1509	1597
$F–CH_2OH$	1507	1602
$F–CH_2OCH_3$	1501	1593
$F–CH_2OC_2H_5$	1501	1594
$F–CH_2OCOCH_3$	1505	1604

$F–CH : CH_2$	1491	1576
$F–CH : CH·COOH$	1483	1577
$F–CH : CH·COOC_2H_5$	1480	1575
F–CO·OR	1478	1572
F–CO·H	1463 1475	1568
F–CO·Cl	1460	1560
F–C ⋮ N	1471	1566

Table 6.

Molecule	ω_9	ω_{10}
α-Methyl-furane, $F–CH_3$	1510	1605
α-Furyl-ethylene, $F–CH : CH_2$	1491	1576
α-Furyl cyanide, F–C ⋮ N	1471	1566

Table 7.

Molecule	ω_9	ω_{10}	Molecule	ω_9	ω_{10}
VII	1503 (1)	1574 (8)	$F–CH_3$	1510 (10)	1605 (6)
VI	1521 (10)	1590 (6)	F–CHO	1475 (10)	1568 (8)
VIII	1523 (10)	1600 (6)	V	1471 (10)	1566 (6)

As shown in Tables 6 and 7, by comparing ω_9 and ω_{10} in α-mono-derivatives of furane with those in the corresponding α, α'-di-derivatives, the following contrasts are pointed out:

(1) In contrast to the α-mono-derivatives mentioned above, two frequencies corresponding to ω_9 and ω_{10}, are argumented in passing from 2, 5-dimethyl-furane to 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5).

(2) The relation of the relative intensities of ω_9 and ω_{10} in α-methy-furane contrasts that in α, α'-dimethyl-furane, while that of ω_9 and ω_{10} in α-furfural and α-furyl cyanide is similar to those in 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5), respectively.

(13) G. B. Bonino and R. Manzoni-Ansidei, *Z. physik. Chem.*, B, **25** (1934), 327.

(3) The values of ω_9 and ω_{10} in α-methyl-furane are slightly higher than those in α, α'-dimethyl furane, while those in α-furfural and α-furyl cyanide are lower than those in 2-methyl-furfural-(5) and 2-methyl-furyl cyanide-(5) by about 50 cm.$^{-1}$

In the case of ethyl 2-methyl-furoate-(3), the Raman lines in question, are found at ω_9 1522 and ω_{10} 1608 cm.$^{-1}$, which may be compared with ω_9 1510 and ω_{10} 1605 in α-methyl-furane and ω_9 1478, ω_{10} 1572 cm.$^{-1}$ in α-furoates. It leads to the conclusion that ω_9 and ω_{10} of 2-methyl-furoate-(3) approach nearer to the values of α-methyl-furane than to those of α-furoates, F–COOR.

In α-furyl-ethylene the Raman lines at $\Delta\nu$ 1642 and 1292 cm.$^{-1}$ are associated with the ethylene linkage of the side chain. The latter may correspond to $\Delta\nu$ 1342 cm.$^{-1}$ in ethylene. The weak lines at $\Delta\nu$ 1507 and 1570 cm.$^{-1}$ in 2-methyl-furyl cyanide-(5) may be attributed to 2-furfuryl cyanide, which is possibly expected from the preparation of the sample from α-furfuryl chloride.

The intense lines at $\Delta\nu$ 183(8), 570(8s) and 2233(10) in α-furyl cyanide, may be associated with the structure of R–C≡N, corresponding to $\Delta\nu$ 170(8b), 549(5) and 2224(12b) in phenyl cyanide, and 376(4), 917(3) and 2250(6) in methyl cyanide.

R–C≡N	ω_1	ω_2	ω_3
CH_3–C≡N	2250 (6)	917 (3)	376 (4)
F–C≡N	2233 (10)	570 (8s)	183 (8)
C_6H_5–C≡N	2224 (12b)	549 (5)	170 (8b)

This estimation is made from the relation of the relative intensities and from the order of the mass of R, when we take R for furyl and phenyl in place of methyl radical.

Summary.

(1) The Raman spectra of the following substances have been measured: α-furfuryl methyl ether, α-furfuryl ethyl ether, α-furfuryl-acetone, α-furyl-ethylene, α-furyl cyanide, 2,5-dimethyl-furane, 2-methyl-furyl cyanide-(5) and ethyl 2-methyl-furoate-(3).

(2) The characteristic frequencies of the α-furfuryl-radical are confirmed. The difference of the Raman spectra of the mono- and di-derivatives of furane is established.

(3) The constitutive influences exerted on the Raman frequencies in the region between $\Delta\nu$ 1400 and 1600 cm.$^{-1}$ are observed.

(4) The Raman lines at 1642 and 1292 cm.$^{-1}$ in α-furyl-ethylene are associated with the structure of R–CH : CH_2, and those at 183, 570, and 2233 cm.$^{-1}$ in α-furyl cyanide with the structure of R–C≡N, when R is taken as furyl radical.

In conclusion, the author wishes to express his thanks to Prof. K. Matsuno for his kind guidance throughout the experiment. The author is indebted also to Ass. Prof. T. Nozoe for his valuable advice in the work of synthesis of the samples. The expense of this experiment was paid from a grant given by the Nippon Gakujutu Sinko Kwai, to which thanks are due.

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THE ABSORPTION SPECTRA OF NITROGLYCERINE.

By Kôiti MASAKI.

Received June 29th, 1936. Published November 28th, 1936.

The absorption spectra of nitroglycerine have been studied with a view to a further study of the modes of photochemical decomposition.

In 1919, Harry Hepworth[1] obtained the absorption spectra of the nitric esters of glycerol to make clear that there is no evidence of chemical isomerism in solution, and that the labile and stable solid forms of nitroglycerine are to be regarded as physical isomerides. And therefore it has been only found that all of the nitric esters of glycerine showed end absorption almost linear between 40000 cm.$^{-1}$ and 47000 cm.$^{-1}$

From the consideration of the some nitrocompounds and nitroesters, the selective absorption of nitroglycerine should appear from the concentration of N/10 in the ordinary thickness (from 1 mm. to 100 mm.) and therefore it could not be discovered by Hepworth, since the solubility in water used by him as a solvent prevented to obtain a concentration higher than N/20000.

The author's investigations have been done for a considerable range of concentration and thickness from 50 cm. of nitroglycerine in liquid to 1 mm. of N/1000 alcoholic solution. The results are in a good agreement with his prediction.

Experimental. The experiments were made with nitroglycerine prepared in the laboratory, washed with successive changes of distilled water, dried in vacuum over solid potassium hydroxide, and finally obtained as a clear, mobile, faint yellow oil which froze at 12.6°C.; sp. gr. 1.5958 at 25°C.

The absorption of a column of nitroglycerine in liquid and in alcoholic solution for a suitable concentration and thickness of layer previously described was examined with Hilger E_2 spectrograph. A hydrogen discharge tube constructed by the author was used as a source of continuous light. Photographic plates employed were the Ilford soft gradation panchromatic plates and the Schumann plates for the short wave length. The time of exposure was five minutes. The results are given in Table 1 and the curve of the absorption is shown in Fig. 1.

(1) *J. Chem. Soc.*, **115** (1919), 840.

Table 1. Nitroglycerine.

Logarithms of thickness				Wave length	Wave number
		log D	log D(3)	λ (Å)	ν (mm.$^{-1}$)
Pure liquid(2)		2.70	7.02	4227	2365
		2.23	6.55	3767	2654
		2.00	6.32	3586	2788
		1.00	5.32	3214	3115
Alcoholic solution	1 N	2.00	5.48	3263	3061
		1.80	5.28	3225	3100
		1.60	5.08	3191	3133
		1.40	4.88	3161	3163
		1.20	4.68	3126	3198
		1.00	4.48	3117	3207
	N/10	2.00	4.48	3117	3207
		1.80	4.28	3076	3250
		1.60	4.08	3031	3298
		1.40	3.88	2973	3363
		1.20	3.68	2907	3439
		1.00	3.48	2838	3523
		0.80	3.28	2748	3639
		0.70	3.18	2696	3708
		0.60	3.08	2612	3827
		0.50	2.98	2493	4010
		0.40	2.88	2449	4082
		0.20	2.68	2405	4157
		0.00	2.48	2374	4211
	N/100	2.00	3.48	2830	3533
		1.90	3.38	2778	3599
		1.70	3.18	2695	3703
		1.50	2.98	2492	4012
		1.40	2.88	2471	4046
		1.20	2.68	2439	4116
		1.00	2.48	2385	4192
		0.70	2.18	2325	4300
		0.50	1.98	2282	4381
		0.20	1.68	2230	4483
	N/1000	2.00	2.48	2384	4193
		1.95	2.43	2370	4218
		1.70	2.18	2325	4300
		1.50	1.98	2285	4376
		1.40	1.88	2272	4400
		1.20	1.68	2230	4483
		0.90	1.38	2178	4590
		0.50	0.98	2105	4749

(2) Since the density of nitroglycerine is 1.60, pure liquid corresponds to 7.05 N.

(3) For convenience of comparison of the spectra, the author took one gram mol divided by the number of NO_2 group for one gram mol; in the case of nitroglycerine it is equal to the molecular wt. divided by 3. see Errata V 11, P. 506

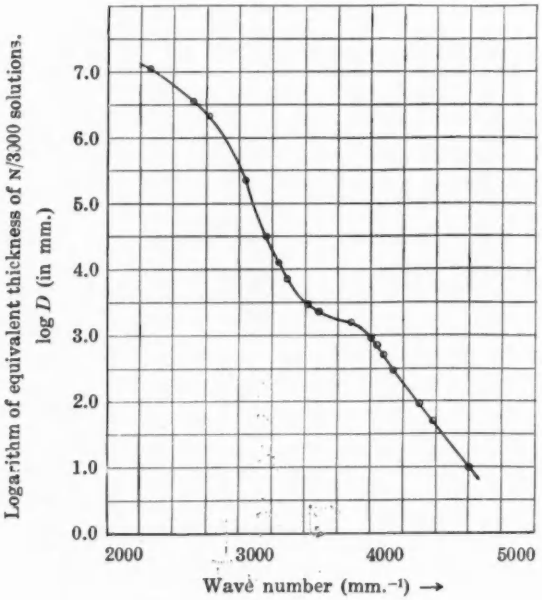

Fig. 1. The Absorption Spectra of Nitroglycerine.

Discussion. The first and probably the second absorption bands of nitroglycerine may be reasonably to attributed to the NO_2-groups in the molecule, since the absorption spectra of the simple nitrocompounds and also nitric esters lacking other special groups (except NO_2) which not only have an absorption at wave length greater than 2000 Å, but also show irregularity of the band owing to the effect of an intense polarity, are quite similar in type. The absorption bands of these compounds, namely, nitromethane,[4][5][6] nitroethane,[4][6][7] nitropropane,[6] 2-nitro-propane,[6] nitrocyclohexane,[6] 1-methyl-1-nitro-cyclopentane,[6] nitric acid,[8] ethyl nitrate,[7] are almost the same at the wave lengths ca. 3200–2500 Å and less than 2500 Å and also similar in the intensity as Table 2 shows.

(4) Baly, *J. Chem. Soc.*, **93** (1908), 1747.
(5) Hedley, *Ber.*, **41** (1908), 1195.
(6) Zelinsky and Rosanoff, *Z. physik. Chem.*, **78** (1912), 629.
(7) J. W. Goodeve, *Trans. Faraday Soc.*, **30** (1934), 504.
(8) P. Bovis, *Ann. phys.*, **10** (1928); *Compt. rend.*, **178** (1924), 1964; *ibid.*, **185** (1928), 57.

Table 2. The 1st Absorption Bands of Nitrocompounds and Nitroesters.

Compound	Wave length (Å)	Max. (Å)	Intensity (log ε)*
Nitromethane	3000—2500	2700	1.2
Nitroethane	3300—2500	2760	1.1
Nitropropane	3100—2500	2760	1.0
2-Nitropropane	3100—2500	2740	1.1
Nitrocyclohexane	3200—2500	2780	1.1
1-Methyl-1-nitrocyclopenthane	3200—2500	2810	1.2
Nitric acid	3100—2500	2700	1.0
Ethyl nitrate	3100—2500	2700	1.0
Nitroglycerine	3300—2500	—	1.0

* ε is the molecular extinction coefficient.

From the results, these two diffused bands common to the nitrocompounds and nitroesters may be attributed to the NO_2-group in which the valency-electronic jumps accompanied by molecular vibration may be expected. The general discussion will be given in another paper.

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CHEMICAL STUDIES ON CANNED MEATS. II. ON THE CONTENTS OF GASES AND METALS IN STORED CANS.

By **Yuzuru OKUDA** and **Kitaro KATAI.**

Received August 20th, 1936. Published November 28th, 1936.

In the first paper[1] on some chemical changes of muscle proteins in canning, we described the changes of *p*H, of the forms of nitrogen and sulphur, of elementary composition, of the contents of arginine, histidine, lysine, cystine, cysteine, tyrosine, tryptophane and proline. The present communication deals with the contents of gases and metals in the cans which have endured long storage.

(1) This Bulletin, **9** (1934), 75.

As a means to know the changes of canned meats and the state of corrosion of can-materials, gases, such as carbon dioxide, hydrogen, oxygen and nitrogen, sometimes ammonia and hydrogen sulphide, together with metals, such as iron and tin, dissolved from cans were determined with the results shown in Tables 1, 2 and 3.

Table 1. Beef. +: present; −: absent

Age of cans (years)	15	7	5	1
No. of analysis	6	7	3	3
Blown cans	+	−	−	−
Corrosion of cans	+++	++	++	+
Putrid odor	−	−	−	−
Appearance of meat	Normal	Normal	Normal	Normal
Contents (g.)	156	159	450	459
Water (%)	61.0	60.5	60.2	59.7
Dry matter ,,	39.0	39.5	39.8	40.3
Gas (c.c.)	79.5	25.9	15.9	10.4
CO_2 (%)	3.4	4.9	3.6	2.8
O_2 ,,	1.3	1.8	3.0	4.7
H_2 ,,	82.2	22.3	22.3	12.2
N_2 ,,	13.2	71.0	71.2	80.4
Fe (mg. %)	191.5	15.6	14.2	13.7
Sn ,,	375.0	219.5	104.5	78.3
*p*H	5.8	5.6	5.8	5.8

Table 2. Crab.

Age of cans (years)	5	3	1
No. of analysis	6	4	6
Contents (g.)	231	221	224
Water (%)	79.2	78.5	80.0
Dry matter ,,	20.8	21.5	20.0
Gas (c.c.)	9.5	7.0	11.0
CO_2 (%)	0.3	0.6	0.4
O_2 ,,	9.6	7.2	10.1
H_2 ,,	11.6	11.9	8.7
N_2 ,,	78.5	80.4	80.8
Fe (mg. %)	10.6	11.3	9.7
Sn ,,	19.9	17.9	15.0
*p*H	6.9	6.9	7.0

Table 3. Salmon and Tunny.

	Salmon		Tunny	
Age of cans (years)	1	7	1	7
Contents (g.)	452	480	404	422
Water (%)	73.7	75.2	62.4	61.1
Dry matter ,,	26.3	24.8	37.6	38.9
Gas (c.c.)	1.5	5.0	21.5	102.0
CO_2 (%)	0	1.8	13.1	5.5
O_2 ,,	6.7	10.2	0.7	0.3
H_2 ,,	35.3	25.0	20.8	73.8
N_2 ,,	58.0	63.0	65.4	20.4
Fe (mg. %)	13.8	16.9	12.7	49.9
Sn ,,	24.2	108.7	87.0	214.8

The results of the experiments carried out with canned meats of different ages of storage, from 1 to 15 years, were as follows:

(1) Among gases contained in cans examined, the quantity of nitrogen was the largest in the majority of the cans, but in some old cans the amount of hydrogen was frequently more than that of nitrogen.

(2) The proportion of oxygen as compared to that of nitrogen was much smaller than it is in the air.

(3) The content of carbon dioxide in cans was larger than that in the air, but it did not increase appreciably during the storage of the cans.

(4) Free ammonia and hydrogen sulphide showed only traces.

(5) The concentration of hydrogen ion of the canned meats showed almost no change in storage.

(6) The contents of iron and tin in both canned beef and fish were nearly proportional to that of hydrogen in the cans which was produced by corrosion of can-materials. But in the case of crab meat packed in the cans which are covered inside with lacquer, almost no increase of the contents of iron, tin and hydrogen was observed.

(7) Unusual increase of hydrogen gas in some very long-stored beef-cans sometimes gave rise to the so-called "blown" cans, in which the ends become convex, and are apparently analogous to the spoiled cans dilated by the pressure of carbon dioxide produced by the action of bacteria upon the contents.

A part of the expense of this investigation was defrayed by a research grant from the "Hattori-Hokokwai", to whom our thanks are due.

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CHEMICAL STUDIES ON CANNED MEATS. III. CARBON DIOXIDE AND HYDROGEN GASES PRODUCED AT CANNING AND IN STORAGE.

By Yuzuru OKUDA and Kitaro KATAI.

Received August 20th, 1936. Published November 28th, 1936.

For the purpose of knowing the changes of canned meat and the state of corrosion of can-materials, we determined oxygen, nitrogen, carbon dioxide and hydrogen gases in commercial cans as described in the preceding paper.[1] In the experiment recorded in the present paper, carbon dioxide was again determined as a means of knowing some chemical changes which occurred in canned meat, and hydrogen gas to know the state of the corrosion of can-material. But in the present case, instead of commercial cans, sealed glass tubes containing a certain meat, tin and iron powders, and solutions of different hydrogen ion concentrations were used for the sake of more exact comparison. The tubes were heated at 130° for different hours, to know the influence of heat and pressure upon canned meat and can-material at canning, and preserved at 50° for different periods to know the effect of storage.

The experiments were performed with three kinds of meats, but only the data with beef are described below, as the results with other meats were analogous.

Table 1. Carbon Dioxide (c.c.)

(a) Sulphuric acid was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
*p*H, before and after heating	4.0—4.5				4.0—4.3			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	2.1	2.6	2.1	3.1	2.2	2.1	1.8	2.7
Sn added	1.4	2.6	2.9	2.2	1.1	1.9	2.5	1.8
Fe and Sn added	2.2	2.2	1.9	3.1	2.0	2.1	1.5	2.8

(1) This Bulletin, **11** (1936), 715.

(b) Water was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
*p*H, before and after heating	5.5—5.7				5.5—5.7			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	1.7	1.2	0.8	2.6	1.7	1.1	1.2	2.5
Sn added	1.5	2.4	2.8	2.3	1.2	2.0	2.4	2.0
Fe and Sn added	1.5	0.5	0.9	2.4	1.4	0.8	0.8	2.4

(c) Sodium hydroxide was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
*p*H, before and after heating	8.5—7.9				8.2—7.9			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	0.9	0.5	0.2	1.8	1.1	0.3	0.2	2.0
Sn added	0.9	1.2	1.3	1.6	1.0	1.4	1.8	1.8
Fe and Sn added	0.9	0.3	0.2	1.4	1.2	0.5	0.2	2.0

Table 2. Hydrogen (c.c.)

(a) Sulphuric acid was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
*p*H, before and after heating	4.0—4.5				4.0—4.3			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	18.6	48.2	57.7	32.5	19.9	55.0	60.1	30.2
Sn added	0.3	0.2	0.2	0.3	0.3	0.3	0.1	0.3
Fe and Sn added	19.7	49.3	57.8	32.8	23.7	54.1	63.3	27.8

(b) Water was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
*p*H, before and after heating	5.5–5.7				5.5–5.7			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	5.2	32.1	36.0	7.4	5.9	34.9	41.1	8.1
Sn added	0.2	0.2	1.2	0.3	0.2	0.1	0.5	0.2
Fe and Sn added	5.2	33.4	33.0	8.7	5.6	40.0	41.6	9.6

(c) Sodium hydroxide was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
*p*H, before and after heating	8.5–7.9				8.2–7.9			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	0.5	16.4	21.5	1.2	1.8	22.9	27.1	5.2
Sn added	0.2	0.1	0	0.2	0	0	0.1	0.2
Fe and Sn added	0.9	17.2	21.2	0.8	1.4	22.1	27.8	5.1

The results of experiments performed with beef and fish were as follows:

(1) The production of carbon dioxide at canning increased a little more, as a rule, in the presence of iron than in the presence of tin alone. And also the longer the time of heating the more was the increase.

(2) The production of carbon dioxide during storage, gradually increased in the presence of tin alone, but decreased in the presence of iron. The decrease seem to be due to the fact that carbon dioxide produced by gradual oxidation acts on iron to make iron carbonate and hydrogen.

(3) The production of carbon dioxide seems to have some relation with the hydrogen ion concentration of meat juice and the kind of meats, but the relation with the freshness of the meat is not definite.

(4) The production of hydrogen is chiefly due to the presence of iron but only slightly to that of tin. In the presence of iron, the production had an

intimate relation with the hydrogen ion concentration of meat juice, the stronger being the concentration the more the production. The production increased proportionally to the length of time of heating at canning, and to the period of storage of cans.

(5) The kind and freshness of meats have more or less influence upon the production of hydrogen from can-material.

(6) The quantity of carbon dioxide produced was generally very small as compared to that of hydrogen.

In conclusion, the authors wish to express their thanks to the "Hattori-Hokokwai" for a research grant from which was defrayed a part of the cost of the investigation.

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SPECTROGRAPHIC METHODS OF STUDYING UNSTABLE COMPOUNDS. II.[1] THE AQUOTIZATION OF TRANS-DICHLORO-TETRAMMINE COBALTIC CHLORIDE IN AQUEOUS SOLUTIONS.

By Ryutaro TSUCHIDA.

Received August 24th, 1936. Published November 28th, 1936.

Introduction. It is well known that trans-dichloro-tetrammine cobaltic salt undergoes a marked colour change[2] in aqueous solutions; its bright green colour fades rapidly away, passes a neutral tint and changes gradually to purple and finally to red. Quantitative measurement of light-absorption of this interesting compound, however, has scarcely been reported. R. Luther and A. Nikolopulos[3] have measured the absorption only in the visible region, and yet the authors themselves acknowledge the inaccuracy of their mearsurement owing to its instability. R. Samuel[4] published an absorption curves as

(1) R. Tsuchida, this Bulletin, **10** (1935), 27.
(2) Y. Shibata, "Spectrochemistry", Vol. I. (1935), 327; *J. Coll. Sci., Imp. Univ. Tokyo,* **37** (1915), Art. 2, 25.
(3) *Z. physik. Chem.*, **82** (1913), 367.
(4) *Z. Physik,* **70** (1931), 54.

that of $[Co(NH_3)_4Cl_2]Cl$[5], but the given absorption is almost identical with that of $[Co(NH_3)_4(H_2O)Cl^{(1)}_{(2)}]Cl_2$, i.e., an aquotization product of both the isomers of dichloro-tetrammine cobaltic chloride. Because of its high reaction velocity, there has been hardly any quantitative investigation on the change of this salt in aqueous solutions, except that of Prof. K. Matsuno[6], who showed the change in its valency effect on the coagulation of arsenious sulphide sol. The mechanism of the change, therefore, has been left to imagination from the analogy of this compound with trans-dichloro-diethylenediamine cobaltic chloride, which has also been investigated by Prof. K. Matsuno[7] by means of his ingenious method of coagulation of arsenious sulphide sol. The change was concluded to be due to the following reactions.

$$[Co\ en_2Cl_2^{(1)}_{(6)}]Cl + H_2O \rightarrow [Co\ en_2Cl\ H_2O^{(1)}_{(6)}]Cl_2$$

$$[Co\ en_2Cl\ H_2O^{(1)}_{(6)}]Cl_2 + H_2O \rightarrow [Co\ en_2(H_2O)_2^{(1)}_{(2)}]Cl_3 .$$

The velocity constants have been given as 0.011 and 0.0031 referring to minute, i.e., 1.9×10^{-4} and 5.2×10^{-5} for second.

The reaction of $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$, however, is too rapid to follow quantitatively by means of the coagulation method or by measuring the electrolytic conductivity. Moreover, the aquotization takes place in the following scheme, as we shall see later.

$$[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl \rightarrow [Co(NH_3)_4ClH_2O^{(1)}_{(6)}]Cl_2$$

$$\swarrow$$

$$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2 \rightarrow [Co(NH_3)_4(H_2O)_2^{(1)}_{(2)}]Cl_3$$

It is obvious that the conductivity of the system is hardly affected by the second reaction and the valency of the ions remains the same during the isomeric change. Then both the conductivity measurement and the coagulation method would be inapplicable for this case. Spectrographic method could be more advantageously applied even for this rapid and complicated reaction. The present author photographed from time to time the absorption spectra of mixed solutions of the praseo-salt and its aquotization products as a whole, and analyzed the absorption at leisure in order to study the kinetics and at the same time to find the extinction coefficients which should belong to the praseo-salt.

Experimental. Trans-dichloro-tetrammine cobaltic chloride was prepared by the the method of S.M. Jörgensen[8]. A weighed portion of this salt was

(5) The configuration of the isomer used in the measurement has not been stated in the original.

(6) *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 11, 12.

(7) This Bulletin, **1** (1926), 133.

(8) *Z. anorg. Chem.*, **14** (1897), 416.

expeditiously dissolved in water to make a 0.0150 mol/l. solution, the moment of dissolution being taken as the starting point of the reaction. This solution was subject to spectrographic analysis by means of a spectrograph equiped with a sector-photometer. The first photographic recording was made 6 minutes after the time of dissolution with an aparture of the sector. Further recordings were made after successive intervals of 2, 4, 8,...minutes, i.e. after 8, 12, 20,....minutes from the starting point, the aparture of the sector being kept at the same angle as in the first recording. Next, with a freshly prepared solution of the same concentration, the absorption spectra were photographed after 6, 8, 12, 20,....minutes from the time of dissolution, the angle of the sector being kept constant throughout the second series of experiments, but different from that for the first. The process was repeated with many a portion, on the same conditions except the aparture of the sector which was varied for each portion. The room temperature was kept at about 17°C. throughout the experiment. The absorption of the mixed solutions were found by measuring the photographic plates, and a set of curves was obtained (Fig. 1).

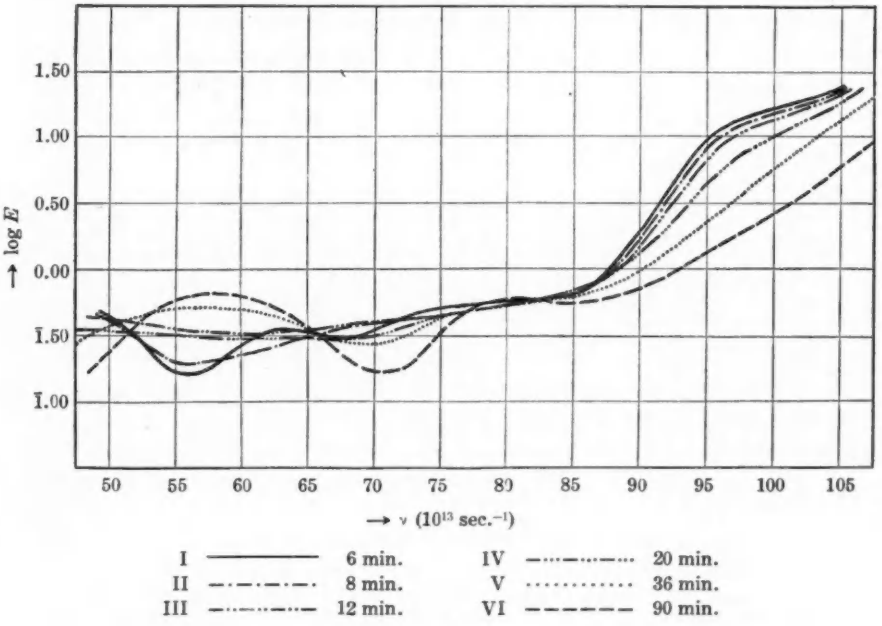


Fig. 1.

E represents $\Sigma\varepsilon c$ in $I = I_0 \times 10^{-d\Sigma\varepsilon c}$, where ε's are molar extinction coefficients, C's, concentrations and d, the thickness of layer. From these curves the following facts may be concluded.

(1) The curve VI, i.e., the absorption after 90 minutes, is almost identical with that of $[Co(NH_3)_4ClH_2O^{(1)}_{(2)}]Cl_2$ (Curve C[9] in Fig. 5), but considerably different from that of $[Co(N_3H)_4(H_2O)_2^{(1)}_{(2)}]Cl_3$ (Curve D[9] in Fig. 5). It can, therefore, be concluded that by this time the aquotization has so far proceeded that only one molecule of water has entered the complex radical and diaquotetrammine cobaltic chloride has not yet been produced in appreciable quantity.

(2) The praseo-salt and its aquotization products have equal molar extinction coefficients for two frequencies 66×10^{13} and 82.5×10^{13}.

(3) The bulges of the curves (I, II, III and IV) at about 96×10^{13} indicate the probable existence of an absorption band belonging to an unstable compound which changes gradually with the disappearance of the bulge.

Analysis and Discussion. Let X and Y be the compounds contained in mixed solutions and the molar extiction coefficients of X and Y for frequencies $\nu_1, \nu_2, \ldots$ be $\varepsilon_1^X, \varepsilon_2^X, \varepsilon_1^Y, \varepsilon_2^Y, \ldots$. Then the following relation exists among the concentrations of X in the mixed solutions, I, II, III, ...

$$\begin{vmatrix} \varepsilon_1^X & \varepsilon_1^Y \\ \varepsilon_2^X & \varepsilon_2^Y \end{vmatrix} = \frac{\begin{vmatrix} E_1^{I} & \varepsilon_1^Y \\ E_2^{I} & \varepsilon_2^Y \end{vmatrix}}{[X]_I} = \frac{\begin{vmatrix} E_1^{II} & \varepsilon_1^Y \\ E_2^{II} & \varepsilon_2^Y \end{vmatrix}}{[X]_{II}} = \frac{\begin{vmatrix} E_1^{III} & \varepsilon_1^Y \\ E_2^{III} & \varepsilon_2^Y \end{vmatrix}}{[X]_{III}} = \ldots . (1),$$

where E's represent the measurable absorptions, the suffixes denoting the solutions and the frequencies. In our case two frequencies, $56 \times 10^{13} (= \nu_1)$ and $82.5 \times 10^{13} (= \nu_2)$ are chosen for practical analysis. For the former frequency, $[Co(NH_3)_4Cl\,H_2O^{(1)}_{(2)}]Cl_2$ has an extinction coefficient nearly equal to the maximum value in its first band, while $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ and $[Co(NH_3)_4Cl\,H_2O^{(1)}_{(6)}]Cl_2$ are supposed to have much smaller values approximately equal to each other. For the latter frequency, $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ and its aquotization products have equal coefficients. The analysis is as follows.

From (1)

$$\frac{E_1^{I} - E_2^{I}\frac{\varepsilon_1^Y}{\varepsilon_2^Y}}{[X]_I} = \frac{E_1^{II} - E_2^{II}\frac{\varepsilon_1^Y}{\varepsilon_2^Y}}{[X]_{II}} = \ldots\ldots\ldots\ldots = a\,. \qquad (2)$$

(9) These complex salts were prepared and studied by Messrs. K. Fukui, S. Seki and M. Kobayashi in this laboratory.

From Fig. 1 we have

$$E_2^{\mathrm{I}} = E_2^{\mathrm{II}} = E_2^{\mathrm{III}} = \cdots\cdots\cdots\cdots \quad .$$

Assuming $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ as Y, we have from Fig. 5

$$\log \varepsilon_1^{\mathrm{Y}} = 1.60 \quad \text{and} \quad \log \varepsilon_2^{\mathrm{Y}} = 1.56 \ ,$$

and from Fig. 1, $E_2 = \bar{1}.78$.

Therefore we get

$$a[\mathrm{X}] = E_2 \frac{\varepsilon_1^{\mathrm{Y}}}{\varepsilon_2^{\mathrm{Y}}} - E_1 = 0.661 - E_1 \quad (3)$$

The values of $\log a[\mathrm{X}]_{\mathrm{I}}$, $\log a[\mathrm{X}]_{\mathrm{II}}$, ... were calculated by (3) and plotted against time resulting a convex curve (Fig. 2).

The curve thus obtained was extrapolated to t_0, at which [X] was 0.0150 mol/l. From $\log a[\mathrm{X}]_{t=0}$, we could estimate [X]'s for the solutions after 6, 8, 12, ... minutes from the time of dissolution.

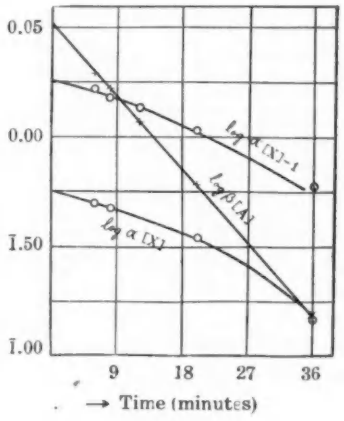


Fig. 2.

Table 1.

	Time (min.)	E_1	a[X]	log a[X]	[X]
I	6	0.159	0.502	$\bar{1}$.701	0.0134
II	8	0.187	0.474	$\bar{1}$.676	0.0126
III	12	0.329	0.332	$\bar{1}$.521	0.0088
IV	20	0.310	0.351	$\bar{1}$.545	0.0093
V	36	0.513	0.148	$\bar{1}$.170	0.0053
VI	90	0.617	0.004	$\bar{2}$.643	0.0012
	0	extrapol.	0.563	$\bar{1}$.750	0.0150

In order to confirm the results, another set of frequencies, $82.5 \times 10^{13} (= \nu_2)$ and $102 \times 10^{13} (= \nu_1)$ was taken for similar analysis. From Fig. 5 and Fig. 1,

$$\log \varepsilon_1^{\mathrm{Y}} = 2.16, \quad \log \varepsilon_2^{\mathrm{Y}} = 1.56 \quad \text{and} \quad \log E_2 = \bar{1}.78.$$

Therefore $\alpha'[X] = E_1 - E_2 \frac{\varepsilon_1^Y}{\varepsilon_2^Y} = E_1 - 2.40$. (3′)

Log $\alpha'[X]$ plotted against time (Fig. 2) gives another convex curve quite similar to log $\alpha[X]$. Extrapolating the curve to t_0, we obtained $\log \alpha'[X]_{t=0}$ from which [X] could be calculated (Table 2).

Table 2.

	Time (min.)	E_1	$\alpha'[X]$	$\log \alpha'[X]$	[X]
I	6	19.1	16.7	1.223	0.0141
II	8	17.4	15.0	1.176	0.0126
III	12	15.9	13.5	1.130	0.0114
IV	20	13.2	10.8	1.033	0.0091
V	36	8.32	5.9	0.771	0.0050
VI	90	2.64	2.2	0.301	0.0002
	0	extrapol.	17.8	1.250	0.0150

From [X] the concentration of $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$, [C], can be found by $[C] = [A]_0 - [X]$.

Table 3.

The Concentration of $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$.

	Time (min.)	From Table 1 (mol/l.)	From Table 2 (mol/l.)	Mean [C] (mol/l.)
	0	0.0000	0.0000	0.0000
I	6	0.0016	0.0009	0.0014
II	8	0.0024	0.0024	0.0024
III	12	0.0062*	0.0036	0.0036
IV	20	0.0057	0.0059	0.0058
V	36	0.0097	0.0100	0.0099
VI	90	0.0138	0.0148	0.0143

* This value is excluded from further calculation because of its deviation.

The concentration of $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ in each case being now known, the contribution of the salt to the light absorption of the reaction mixture

can be calculated from the concentration (Table 3) and its extinction coefficients (Curve C in Fig. 5), and is subtracted from the absorption of the corresponding mixed solution. The residual absorption, i.e., the absorption, due to compounds other than $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ is shown in Fig. 3, where $E - \varepsilon^c[C]$ is represented by F.

It is evident from this set of curves that the solutions are still mixtures, as we can easily point out at least three different absorption bands, of which one with the frequency of 65×10^{13} and another of about 10×10^{14} gradually disappear as the reaction proceeds, while the band at 75×10^{13} becomes more and more distinct. If $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ and $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ were the only constituents of the mixed solutions, such gradual change of F would never be seen, but a set of curves with an identical shape and different heights should result after the analysis. Moreover, if the praseo-salt were to change directly to the cis-aquochloro-salt as a reaction of the first, or of the higher, order, the curves of $\log a[X]$ and $\log a'[X]$ should be straight, or concave upwards. We have, however, seen that the curves are convex upwards (Fig. 2). This feature of the curves may be explained, if we assume that the praseo-salt, A, changes first to an intermediate compound, B, and then to the cis-aquochloro-salt, C. Then $\log([A]+[B])$ will give a curve convex upwards. Another fact also indicates that some compound must intervene between A and C; in spite that the colour of the praseo-salt had almost completely disappeared in 30 minutes, the absorption of the cis-aquochloro-salt alone was not seen till after 90 minutes. The absorption curves in Fig. 3, therefore, represent mixed solutions of $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ and the intermediate compound. Whatever the constitution of the latter may be, the analysis of the curves may be done as follows. For this purpose the extinction coefficients of at least one of the salts must be known, but we know none of them: B is an unknown substance and A is the compound whose extinction coefficients are searched for. For practical purpose, however, we may assume without much risk that after 36 minutes from the time of dissolution the praseosalt had completely disappeared, as was shown by the colour of the solution.

Then
$$F_1^V \simeq \varepsilon^B[B] \quad . \tag{4}$$

Then frequencies 76×10^{13} $(= \nu_1)$ and 96×10^{13} $(= \nu_2)$ were chosen for analysis.

From (1)
$$\begin{vmatrix} \varepsilon_1^A & \varepsilon_1^B \\ \varepsilon_2^A & \varepsilon_2^B \end{vmatrix} = \frac{\begin{vmatrix} F_1^I & \varepsilon_1^B \\ F_2^I & \varepsilon_2^B \end{vmatrix}}{[A]_I} = \frac{\begin{vmatrix} F_1^{II} & \varepsilon_1^B \\ F_2^{II} & \varepsilon_2^B \end{vmatrix}}{[A]_{II}} = \cdots\cdots \tag{1'}$$

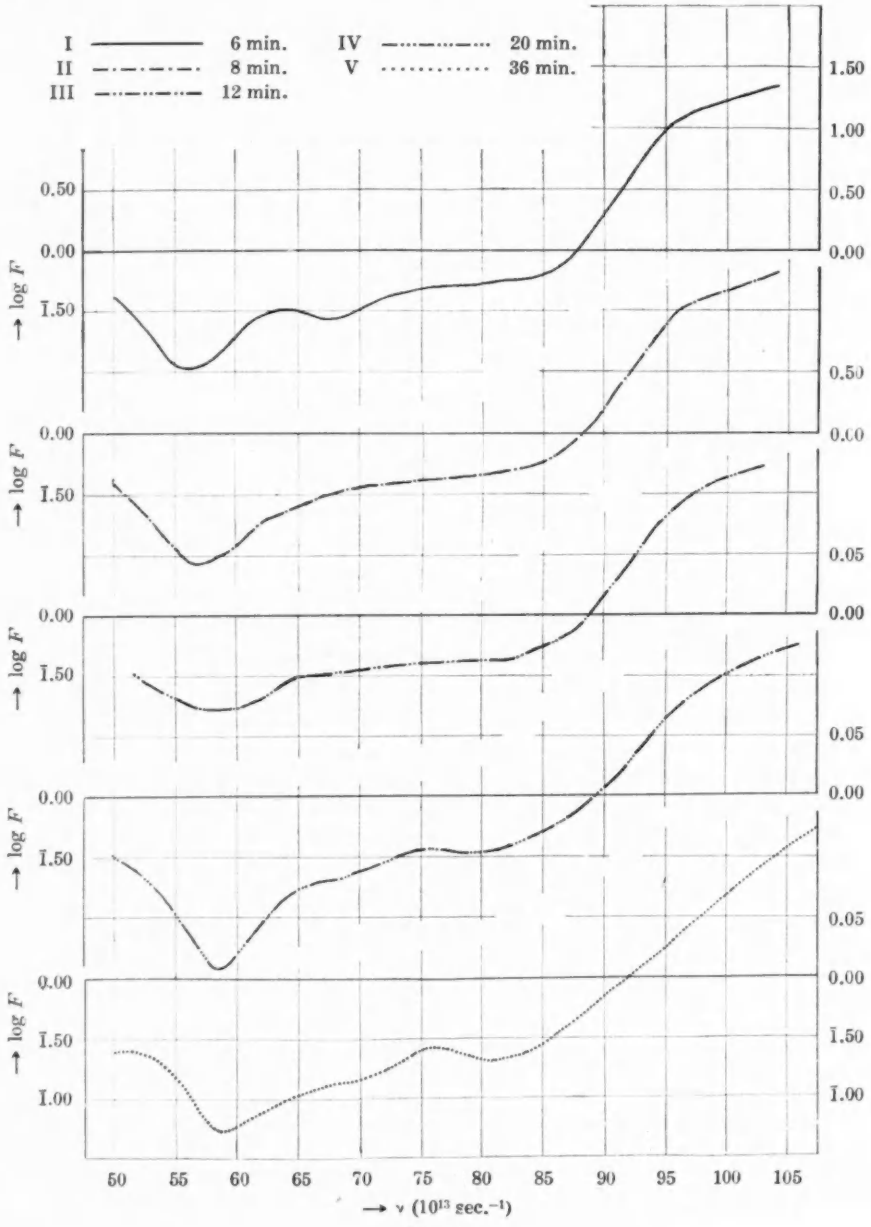

I 6 min.
II 8 min.
III 12 min.
IV 20 min.
V 36 min.
→ log F
0.50
0.00
1.50
1.00
0.05
1.00
50
55
60
65
70
75
80
85
90
95
100
105
→ ν (10¹³ sec.⁻¹)

Fig. 3.

We get from (4) and Table 3,

$$F_1 \simeq 0.0051\,\varepsilon_1^{B} \quad \text{and} \quad F_2 \simeq 0.0051\,\varepsilon_2^{B}.$$

$$\therefore \quad \beta = \frac{F_1^{I}F_2^{V} - F_2^{I}F_1^{V}}{[A]_I} = \frac{F_1^{II}F_2^{V} - F_2^{II}F_1^{V}}{[A]_{II}} = \cdots\cdots\cdots\cdots \qquad (5)$$

When $\log \beta[A]$ thus calculated by (5) was plotted against time, a straight line was obtained (Fig. 2). This shows that the change of the praseo-salt into B is a reaction of the first order. Extrapolating this straight line, we obtain $\log \beta[A]_{t=0}$ which corresponds to the initial concentration of $[Co(NH_3)_4Cl_{2(6)}^{(1)}]Cl$, i.e., 0.0150 mol / l. Hence [A] in each of the mixed solutions can be calculated as in Table 4.

Table 4.

The Concentration of $[Co(NH_3)_4Cl_{2(6)}^{(1)}]Cl$.

	Time (min.)	log F_1	log F_2	$F_1F_2^{V} - F_2F_1^{V}$	log β[B]	[A] (mol/l.)
I	6	$\bar{1}.698$	1.057	1.92	0.283	0.0088
II	8	$\bar{1}.613$	0.996	1.68	0.225	0.0077
III	12	$\bar{1}.600$	0.902	1.21	0.082	0.0056
IV	20	$\bar{1}.547$	0.724	0.61	$\bar{1}.785$	0.0028
	0	extrapolated		3.27	0.515	0.0150
	36	,,		0.15	$\bar{1}.180$	0.0007

The concentration of B can be found by $[B] = [A]_0 - [A] - [C]$, from Tables 3 and 4.

As to the constitution of the intermediate compound B, there are two possible cases to be considered.

	A	B	C
(1)	$[Co(NH_3)_4Cl_{2(6)}^{(1)}]Cl$	$[Co(NH_3)_4Cl_{2(2)}^{(1)}]Cl$	$[Co(NH_3)_4Cl\ H_2O_{(6)}^{(1)}]Cl_2$
(2)	,,	$[Co(NH_3)_4Cl\ H_2O_{(6)}^{(1)}]Cl_2$	,,

Prof. Matsuno's research[10] on $[Co\ en_2Cl_{2(6)}^{(1)}]Cl$ favours the second case, and as we shall see later, kinetic considerations and the absorption spectra also support the view.

(10) *Loc. cit.*

The aquotization reaction of trans-dichlorotetrammine cobaltic chloride, therefore, can be shown by the following formulæ.

(1) $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl + H_2O \rightarrow [Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$.

(2) $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2 + H_2O \rightarrow [Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2 + H_2O$.

(3) $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2 + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2^{(1)}_{(2)}]Cl_3$.

As to the third reaction[11] it is not certain whether it proceeds in the sense of the arrow irreversibly or reversibly. Whichever the case may be, the above calculations are scarcely affected by the third reaction, because the two complex salts concerned in it have quite similar absorption curves (Fig. 5).

Kinetics. From the above calculations and discussions, the first and the second reactions may be expressed by the following equations.

$$\frac{d[B]}{dt} = k_1[A] \quad \text{and} \quad \frac{d[C]}{dt} = k_2[B].$$

Hence
$$[A] = [A]_0\, e^{-k_1 t}\ , \tag{6}$$

$$[B] = \frac{k_1[A]_0}{k_1 - k_2}(e^{-k_1 t} + e^{-k_2 t})\ , \tag{7}$$

and
$$[C] = \frac{[A]_0}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\ . \tag{8}$$

From [A] in Table 4, k_1 is calculated by means of (6) (Table 5).

Table 5.

The Velocity Constant k_1.

Time (sec.)	[A] (mol/l.)	k_1 at 17°C.
6×60	0.0088	1.48×10^{-3}
8× ,,	0.0077	$1.39\times$,,
12× ,,	0.0055	$1.37\times$,,
20× ,,	0.0028	$1.40\times$,,
36× ,,	0.0007	$1.31\times$,,
	Mean value	1.39×10^{-3}

Table 6.

The Velocity Constant k_2.

Time (sec.)	[B] (mol/l.)	k_2 at 17°C.
8×60	0.0049	8.1×10^{-4}
12× ,,	0.0058	$10.5\times$,,
20× ,,	0.0064	$9.3\times$,,
36× ,,	0.0044	$8.3\times$,,
	Mean value	9.05×10^{-4}

(11) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 127; *ibid.*, **38** (1917), 696; J. N. Brönsted, *Z. physik. Chem.*, **122** (1926), 392; *J. Am. Chem. Soc.*, **49** (1927), 439.

The velocity constant k_2 is calculated by means of (7), k_1, [A] and [B] being now known (Tables 3, 4 and 5).

The concentrations of the three salts are calculated from (6), (7) and (8), substituting k_1 and k_2 thus found.

Table 7. Concentrations of the Compounds contained in the Mixed Solutions.

Time (min.)	$[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ (mol/l.)		$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}Cl_2]$ (mol/l.)		$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ (mol/l.)	
	Found	Calc.	Found	Calc.	Found	Calc.
0	0.0150	0.0150	0.0000	0.0000	0.0000	0.0000
6	0.0088	0.0092	0.0048	0.0046	0.0014	0.0012
8	0.0077	0.0076	0.0049	0.0055	0.0024	0.0019
12	0.0056	0.0055	0.0058	0.0063	0.0036	0.0032
20	0.0028	0.0028	0.0064	0.0062	0.0058	0.0050
36	0.0007	0.0008	0.0044	0.0038	0.0099	0.0104
90	0.0000	0.0000	0.0007	0.0003	0.0143	0.0147

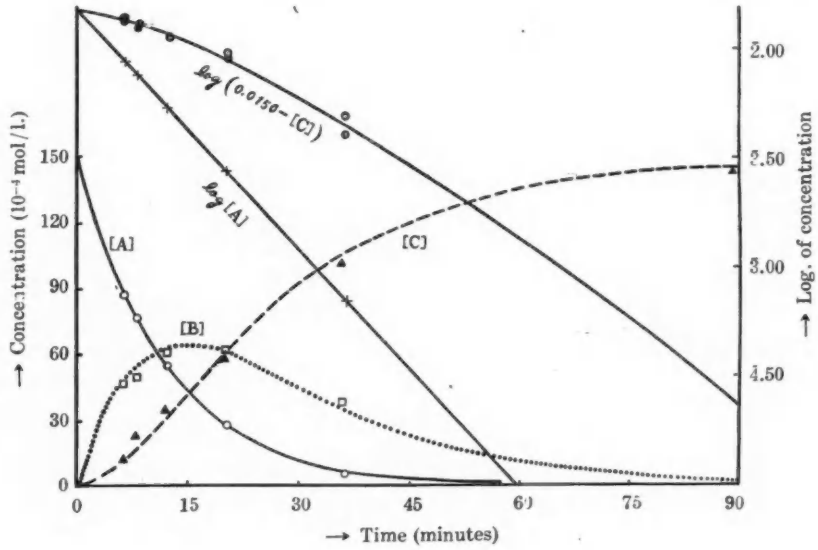


Fig. 4.

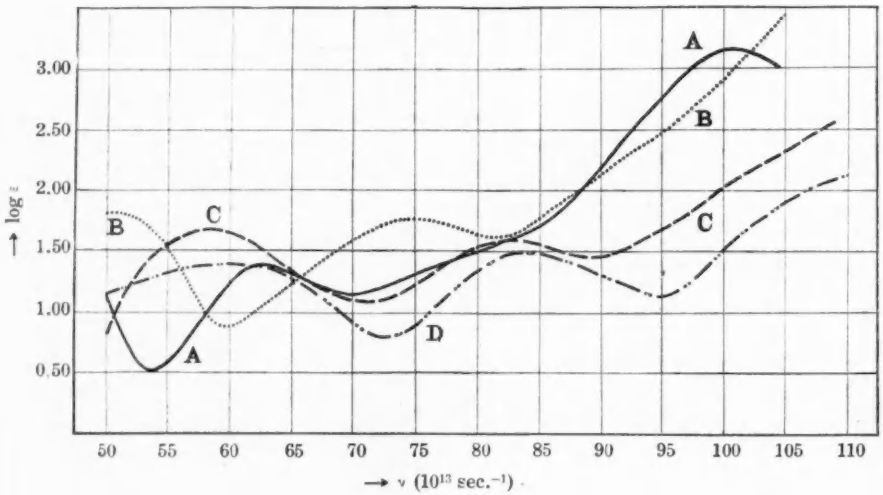
The results are summarized in Fig. 4 in which the smooth curves show the calculated values.

The maximum value of [B] is attained at

$$t_{max.} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} \quad . \tag{10}$$

The results of the analysis show that the maximum value is attained at a point between 12 and 20 minutes, while the calculation by (10) gives 15 minutes.

Absorption Curves of $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ and $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$. Trans-aquochloro-tetrammine cocaltic salt has never been reported. Trans-dichloro-tetrammine cobaltic saltic salt can never exist alone in aqueous solutions and consequently its absorption has never been observed without superposition of those of its aquotization products. In order to find molar extinction coefficients of these very unstable complex compounds, the curves I and V in Fig. 1 were again analysed making use of the calculated concentrations in Table 7. The results are shown in Fig. 5, together with the absorption curves of $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ and $[Co(NH_3)_4(H_2O)_2^{(1)}_{(2)}]Cl_3$.



A ——— $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ C – – – – – – $[Co(NH_3)_4H_2O\ Cl^{(1)}_{(2)}]Cl_2$

B ····· $[Co(NH_3)_4H_2O\ Cl^{(1)}_{(6)}]Cl_2$ D —·—·—·— $[Co(NH_3)_4(H_2O)_2^{(1)}_{(2)}]Cl_3$

Fig. 5.

The selective absorption bands of these complex salts are given in Table 8.

Table 8.

	The first band		The second band		The third band	
	ν	log ε	ν	log ε	ν	log ε
$[Co(NH_3)_4Cl_2^{(1)}_{(5)}]Cl$	$<50\times10^{13}$	1.2	62.5×10^{13}	1.37	10×10^{14}	3.16
$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$	50 ,,	1.3	74.5 ,,	1.76	—	—
$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl$	58.5 ,,	1.67	82.5 ,,	1.59	—	—
$[Co(NH_3)_4(H_2O)_2^{(1)}_{(2)}]Cl_3$	60 ,,	1.40	84 ,,	1.49	—	—

The first and the second band of $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$ is of higher frequency than the corresponding band of $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$. In other words, the substitution of the Cl ion in the co-ordination by H_2O molecule shows a hypsochromic effect. Similar effect is observed when Cl in $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ is substituted by H_2O.

One of the most remarkable features of the absorption curve of the praseo-salt is that it has three absorption bands, of which the third is of interest. Generally speaking, most complex salts have two selective absorption bands in the visible and the near-ultraviolet regions and it has been known that only a few trans-dinitro-complex compounds such as $[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]Cl$[12], $[Co(NH_3)_3(NO_2)_3]$[12], $[Co(NH_3)_2(NO_2)_4]NH_4$[12], $[Co(NH_3)_3(NO_2)_2Cl]$[13] and $[Co(NH_3)_3(NO_2)_2Br]$[13], and some rhodanatoammine complex salts[14] show the third absorption bands. The author should like to predict that the third band is one of the general characteristics of those complex compounds which have at least one pair of ions co-ordinated in trans-position to each other. In order to confirm this view, Mr. S. Kashimoto[15] in this laboratory has recently examined $[Co(NH_3)_4NO_2Cl]Cl$ and $Na_3[Co(NO_2)_6]$ and found that they have also the third absorption bands.

(12) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(13) M. Kobayashi, A. Hagitani, and I. Mita, *ibid.*, **57** (1935), 500.

(14) Y. Shibata and K. Matsuno, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 9.

(15) The results shall soon be published.

Summary.

(1) A new complex compound $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$ was found by the spectrographic analysis.

(2) Trans-dichloro-tetrammine cobaltic chloride in aqueous solutions changes in the following scheme:

$$[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl \rightarrow [Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$$

$$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2 \rightarrow [Co(NH_3)_4(H_2O)_2]Cl_3$$

(3) The velocity constants of the first two reactions were found to be 1.39×10^{-3} and 9.05×10^{-4} respectively.

(4) The absorption curves were found for the unstable complex salts $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ and $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}]Cl_2$, both of which can never exist in acqueous solutions without contamination of related compounds.

(5) The praseo-salt shows a third absorption band of the same type as that of $[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]Cl$.

(6) The third absorption band is supposed to be one of the general characteristics of those complex salts which have in the co-ordination at least one pair of ions in trans-positions to each other.

(7) Substitution of Cl in $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]Cl$ or $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ by H_2O, has hypsochromic effect.

The author wishes to express thanks to Prof. Y. Shibata for his kind interest and to Messrs. M. Kobayashi and N. Shigematsu for their assistance in the experimental work.

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DIHYDROXYSTEARIC ACID IN CASTOR OIL.*

By Yoshiyuki TOYAMA and Tokuzo ISHIKAWA.

Received August 10th, 1936. Published November 28th, 1936.

The presence of a dihydroxystearic acid $C_{18}H_{36}O_4$ melting at 141–143° as a minor constituent in castor oil was first pointed out by Juillard.[1] Since then Haller,[2] Meyer,[3] Eibner and Münzing,[4] Myddleton, Berchem and Barrett,[5] Panjutin and Rapoport,[6] Heiduschka and Kirsten[7] also found this acid in castor oil, but there has been lacking of investigation in detail on this acid, and its constitution remained quite unknown. Lewkowitsch[8] stated in his classical work that this acid—being a natural product—is probably optically active, but this interesting account seemed to be overlooked by subsequent investigators, and there has been no work containing the optical rotation of this acid.

A few years ago we found that methyl or ethyl esters prepared by the methanolysis or ethanolysis of castor oil deposited a minor quantity of laminar crystals at the room temperature in winter, which were confirmed to consist mainly of methyl or ethyl ester of dihydroxystearic acid by examining their characteristics. Afterward we were supplied with a sufficient quantity of crystalline deposit which was separated from the methyl ester of castor oil by the courtesy of the Taisho Kagaku Kogyo K.K. From this crystalline deposit, dihydroxystearic acid was obtained in a pure state, and its properties were examined with a special reference to the constitution and the optical rotation. For the determination of the constitution of dihydroxystearic acid, it was oxidised with sodium bichromate and sulphuric acid, and *n*-nonoic acid $CH_3{\cdot}(CH_2)_7{\cdot}COOH$ and azelaic acid $HOOC{\cdot}(CH_2)_7{\cdot}COOH$ were identified among the oxidation products. Hence the dihydroxystearic acid was found to be 9,10-dihydroxystearic acid having the formula $CH_3{\cdot}(CH_2)_7{\cdot}CHOH{\cdot}CHOH{\cdot}(CH_2)_7{\cdot}COOH$. This formula was verified also in another way; methyl dihydroxystearate was converted into methyl dibromostearate by the action of

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **57** (1936), 976.

(1) *Bull. soc. chim.*, [3], **13** (1895), 238.
(2) *Compt. rend.*, **144** (1907), 462.
(3) *Arch. Pharm.*, **235** (1897), 184.
(4) *Chem. Umschau Fette, Öle, Wachse Harze*, **32** (1925), 153, 166.
(5) *J. Am. Chem. Soc.*, **49** (1927), 2264.
(6) *Chem. Umschau Fette, Öle, Wachse Harze*, **37** (1930), 130.
(7) *Pharm. Zentralhalle*, **71** (1930), 81.
(8) "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Edition, Vol. I, p. 226.

hydrogen bromide, the latter was debrominated, and the octadecenoic acids were liberated on saponification followed by acidulation of the debrominated product. The octadecenoic acids thus obtained were found to be a mixture of two geometrical isomerides (oleic and elaidic acids) of $\Delta^{9:10}$-octadecenoic acids. The optical rotation of dihydroxystearic acid was examined in methanol or chloroform by using a 40 cm. tube, and the solutions were found to be slightly dextro-rotatory, but an accurate measurement was difficult due to an extremely small angle of rotation.[9] Solutions of methyl dihydroxystearate showed also very small dextro-rotation, but the determination of the angle of rotation was difficult.

The acetylated product of methyl or ethyl ester of dihydroxystearic acid was a liquid at the ordinary temperature, and the specific rotation was measured without using solvent; $[\alpha]_D^{30}$ +0.19° for diacetyl ester of methyl dihydroxystearate and $[\alpha]_D^{30}$ +0.31° for diacetyl ester of ethyl dihydroxystearate.

It is thus confirmed by the foregoing results that dihydroxystearic acid in castor oil is *d*-9,10-dihydroxystearic acid. As for the racemic 9,10-dihydroxystearic acid derived from $\Delta^{9:10}$-octadecenoic acids (oleic and elaidic acids), there are known two isomerides. The one melts at 130° and is obtained from oleic acid by Hazura's oxidation method; the other melts at 100° and is obtained from elaidic acid by Hazura's oxidation method. Resolution of these racemic acids into optically active isomerides has hitherto been studied by Freundler[10] and Inoue and Suzuki.[11] Freundler resolved 9,10-dihydroxystearic acid of higher melting point into optically active isomerides by means of its strychnine salt. Ethyl ester of *d*-isomeride had m.p. 98–99° and $[\alpha]_D$ +1.6°, while ethyl ester of *l*-isomeride had m.p. 98–99° and $[\alpha]_D$ −2.1°. Since, however, the solubility of both isomerides was very small, the specific rotation was not measured accurately, and the above figures were stated to show only approximate values. Also Inoue and Suzuki resolved 9,10-dihydroxystearic acids derived from oleic and elaidic acids by means of strychnine salt. The specific rotation observed by these authors were as follows: $[\alpha]_D$ +23.20° and −23.60° for *d*- and *l*-isomerides obtained from 9,10-dihydroxystearic acid of m.p. 130°; $[\alpha]_D$ +27.60° and −27.45° for *d*- and *l*-isomerides obtained from 9,10-dihydroxystearic acid of m.p. 100°. The melting points of optically active isomerides were not recorded in their paper.

(9) The angle of rotation greater than 0.25° was clearly discriminated by the polariscope used, but a 4% solution of dihydroxystearic acid in a 40 cm. tube showed an angle of rotation smaller than +0.25°, and it was difficult to measure it accurately. Roughly speaking, the specific rotation of dihydroxystearic acid should not be greater than +1.6° (0.25÷4÷0.04).

(10) *Bull. soc. chim.*, [3], **13** (1895), 1052.

(11) *Proc. Imp. Acad.* (Tokyo), **7** (1931), 261.

In comparison of *d*-acid separated from castor oil in these experiments and *d*-acids obtained from racemic 9,10-dihydroxystearic acids by the above cited authors, *d*-acid obtained by Freundler has an appreciably lower melting point than *d*-acid of castor oil, while *d*-acids obtained by Inoue and Suzuki show exceedingly greater specific rotations than *d*-acid of castor oil. After it has been confirmed in these experiments that *d*-acid of castor oil is 9,10-dihydroxystearic acid and its specific rotation is very small (not exceeding +1.6°), the discrepancy between the results of our experiments on *d*-acid of castor oil and those of above cited authors on *d*-acids obtained from racemic 9,10-dihydroxystearic acid is not explainable. In order to gain a fuller information regarding this point, we have prepared racemic 9,10-dihydroxystearic acid by oxidation of oleic acid and attempted to resolve it into optically active isomerides by means of its strychnine salt. For the preparation of the strychnine salt of dihydroxystearic acid, strychnine nitrate was added to an alcoholic solution of potassium dihydroxystearate following the method of Freundler with a modification that strychnine nitrate instead of sulphate was used in our experiment. In another experiment dihydroxystearic acid and free strychnine were heated in chloroform solution following the method of Inoue and Suzuki. It was, however, found that no substantial amount of strychnine and dihydroxystearic acid combined by these methods, and the products contained large amount of free strychnine and dihydroxystearic acid. Resolution of dihydroxystearic acid as its strychnine salt was not attained. It should also be noted here regarding the stability of *d*-acid separated from castor oil. According to Inoue and Suzuki the optically active isomerides obtained from racemic 9,10-dihydroxystearic acids had a strong tendency to undergo racemisation. When they were heated in alcoholic solutions for 30 minutes they were completely converted into racemic compounds. Aqueous solutions of their potassium salts were quite inactive. Similar facts were reported by Grün[12] in the case of *d*-isomeride (m.p. 90°) obtained from racemic 9,12-dihydroxystearic acid. Its alcoholic solution became inactive on standing for some time; on heating at 130–140° it became rapidly inactive. The *d*-acid of castor oil is, however, very stable. Even after prolonged heating of its alcoholic solution, the crystals separated on cooling showed the same melting point. After the elapse of several months the melting point of dihydroxystearic acid remained unaltered. Even when dihydroxystearic acid of castor oil was converted into its methyl or ethyl ester and then reconverted into free acid by saponification followed by acidification, there was no indication of racemisation. It is thus seen that contrary to the observations of previous investigators on the optically active isomerides obtained by the resolution of

(12) *Ber.*, **39** (1906), 4400.

racemic compounds, the *d*-acid of castor oil is quite stable and shows no tendency to undergo racemisation.[13]

Experimental.

1. Separation of Dihydroxystearic Acid. The starting material used in these experiments was supplied by the courtesy of the Taisho Kagaku Kogyo K.K. It was a crude deposit which was separated in a yield of ca. 3% from the methyl esters prepared by the methanolysis of castor oil on cooling at 0–5°. Since the removal of the liquid esters was incomplete, the crude deposit formed a pasty mass at the ordinary temperature. In these experiments 1 kg. of the crude deposit was first mixed with 1 l. of methanol and after heating on the water bath for a short time, a small amount of flocculent precipitate was removed by filtration. The clear solution was allowed to stand at the room temperature, and the crystalline deposit was filtered off. The filtrate formed a further quantity of crystalline deposit on ice-cooling. The crystalline deposits thus obtained were united and redissolved in 1 l. of methanol by warming. A small amount of flocculent precipitate was again removed by filtration, and the clear solution was ice-cooled to separate the crystalline deposit which was filtered and treated with methanol as before. After repeating the methanol treatment five times there were obtained finally 89 g. of methyl dihydroxystearate in lustrous laminar crystals which had m.p. 111–112°[14] and saponification value 167.5 (calc. for methyl dihydroxystearate $C_{19}H_{38}O_4$: 170.9). The optical rotation of methyl dihydroxystearate was examined in a 4% solution in methanol by using a 40 cm. tube, but an accurate measurement was difficult due to an extremely small dextro-rotation (less than +0.25°).

On heating methyl dihydroxystearate with twice its weight of acetic anhydride at 140° for 2 hours and subsequently washing the product with boiling water, diacetyl ester $C_{19}H_{36}O_2(OCOCH_3)_2$ was obtained. It formed a colourless liquid and had the following constants : d_4^{15} 0.9826, n_D^{15} 1.4498, $[MR_L]_D$ 113.3 (calc. 113.4), $[\alpha]_D^{20}$ +0.19°, saponif. value 403.7 (calc. 408.2).

For the preparation of dihydroxystearic acid the methyl ester was saponified with alcoholic potash, the product was diluted with water and then acidulated with hydrochloric acid. The dihydroxystearic acid liberated was separated by filtration, washed with water and recrystallised from ether-alcohol (1 : 1), yielding laminar crystals; m.p. 142-143°, neutralisation value 177.5 (calc. for $C_{18}H_{36}O_4$: 177.4). A 1% solution in chloroform and a 4% solution in methanol showed only a very slight rotation in a 40 cm. tube, but the determination of specific rotation was difficult due to an extremely small angle of rotation.

Dihydroxystearic acid was dissolved in alcohol, and after addition of a small amount of sulphuric acid the solution was refluxed on the water bath in order to complete esterification. The product was taken up with ether, the ethereal solution was first washed with a solution of potassium carbonate in order to remove sulphuric acid and unchanged dihydroxy-

(13) S. Ishikawa and G. Maeda presented a paper at the 29th meeting of the Institute of Physical and Chemical Research held on May 22, 1936, in which the separation of methyl dihydroxystearate from commercial methyl ester of ricinoleic acid and the constitution of this dihydroxystearic acid were dealt with. According to these authors this acid seems not to be 9, 10-dihydroxystearic acid. The present investigation showed, however, that the dihydroxystearic acid of castor oil is *d*-9,10-dihydroxystearic acid, but the presence of any other dihydroxystearic acid was not ascertained.

(14) Juillard (*loc. cit.*) gave m.p. 104–106°. Haller (*loc. cit.*) gave m.p. 107–108°.

stearic acid as their potassium salts. The ethereal solution was then washed thoroughly with water, and after distilling off a portion of the solvent from the solution, it was allowed to cool when the crystals of ethyl dihydroxystearate $C_{20}H_{40}O_4$ separated; m.p. 104–105°, saponif. value 161.9 (calc. 162.9).

Diacetyl ester of ethyl dihydroxystearate $C_{20}H_{38}O_2(OCOCH_3)_2$ was obtained by heating ethyl dihydroxystearate with acetic anhydride. It formed a colourless liquid having the following constants: d_4^{15} 0.9743, n_D^{15} 1.4485, $[MR_L]_D$ 117.8 (calc. 118.0), $[\alpha]_D^{30}$ +0.31°, saponif. value 392.6 (calc. 392.9).

2. **Oxidation of Dihydroxystearic Acid.** Fifteen grams of dihydroxystearic acid was mixed with 30 g. of sodium bichromate, 75 g. of sulphuric acid and 300 g. of water, and the mixture was heated in an oil bath, the temperature of which was kept at 110°, for 30 minutes and then subjected to steam distillation by which about 1 l. of distillate was collected. The distillate (a) consisted of a minor proportion of oily substances together with aqueous solution. The residue (b) from steam distillation was a dark green liquid. The distillate was saturated with sodium chloride and shaken with petroleum ether. The petroleum ether solution was separated, and after distilling off petroleum ether there remained 6.4 g. of colourless oil which had d_4^{15} 0.9038, n_D^{15} 1.4336, $[MR_L]_D$ 45.53 (calc. for $C_9H_{15}O_2$: 45.30), neutral. value 350.8 (calc. for $C_9H_{15}O_2$: 354.8). This oil was converted into the acid chloride by heating with thionyl chloride on the water bath. The acid chloride formed was dropped into ice-cooled ammonia and the precipitated acid amide was filtered and washed with water. It was dissolved in 50% alcohol, treated with active carbon and cooled down to separate the crystals which were identified with *n*-nonoic acid by its m.p. and mixed m.p. 98.5–99°.

The residue (b) from steam distillation was shaken with 2 l. of ether. The ethereal solution was separated and after washing with saturated brine the ether was distilled off leaving 4 g. of bluish-green coloured crystalline solid as residue. This was dissolved in boiling water, in which a small amount of green coloured substances remained insoluble. The clear solution was separated and cooled down to deposit laminar crystals which on recrystallisation from water gave pure azelaic acid; yield 2 g., m.p. 106–107°, neutr. value 593.0 (calc. for $C_9H_{16}O_4$: 596.5). It showed no depression of melting point when admixed with an authentic specimen of azelaic acid.[15]

3. **Preparation of Oleic and Elaidic Acids from Methyl Dihydroxystearate.** Ten grams of methyl dihydroxystearate was heated in a flask for 30 minutes by means of an oil bath, the temperature of which was kept at 140°. During heating a current of hydrogen bromide was passed through the melted mass. The methyl dibromostearate thus formed was a viscous oil. Ten c.c. of methanol and 13 g. of zinc powder were added to the product and the mixture was refluxed on the water bath. Ten c.c. of 5 N hydrogen chloride in methanol was added in the course of 20 minutes, and the heating was continued for another 20 minutes, after which the product was taken up with ether. The ethereal solution was washed with water, the ether was distilled off, and the residue consisting of methyl octadecenoate was saponified with alcoholic potash. The soap solution was acidified with

(15) The specimen of azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid and had m.p. 105–106°. Azelaic acid obtained in these experiments from dihydroxystearic acid in castor oil is believed to have a higher purity than the specimen from oleic acid.

hydrochloric acid, and the separated free acids were taken up with petroleum ether. The petroleum ether solution was washed with water, the solvent was distilled off, and there remained 8 g. of residue which had neutral. value 196.0, iodine value 84.1 and m.p. 35–36°. On cooling the solution of the residue in 80% alcohol, there was formed about 5 g. of crystalline solid which yielded on recrystallisation from 80% alcohol crystals having neutral. value 198.7 (calc. for $C_{18}H_{34}O_2$: 198.8), iodine value 87.6 (calc. for $C_{18}H_{34}O_2$: 89.9) and m.p. 44.5–45°. No depression of melting point was observed when this substance was added to an authentic specimen of elaidic acid.[16] The mother liquor separated from crystals of elaidic acid contained a liquid fatty acid which deposited only a minute amount of solid after standing for several days at the room temperature. The liquid portion was found to consist of oleic acid, since it was converted into a solid mass by the action of nitrous acid and the latter yielded after purification elaidic acid having neutral. value 197.1, iodine value 88.3 and m.p. 44.5–45°.

4. **Preparation of Dihydroxystearic Acid from Oleic Acid and Attempt to Resolve it into Optically Active Isomerides by Means of its Strychnine Salt.** Fifteen grams of oleic acid prepared from tsubaki oil was mixed with 18 c.c. of potassium hydroxide solution (ca. 28%) and then diluted with 1 l. of water. To this solution of potassium oleate, 1 l. of potassium permanganate solution (1.5%) was gradually added with constant stirring, and then sulphur dioxide was passed through the solution until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. Dihydroxystearic acid was separated by filtration, and after being washed with water it was recrystallised from 95% alcohol yielding 11.2 g. of crystals having m.p. 129.5–130°. By repetition of these operations a further quantity of dihydroxystearic acid was prepared.

Thirty-six grams of dihydroxystearic acid and 45 g. (ca. 20% in excess) of strychnine were refluxed on the water bath when a clear solution was obtained. After heating for 30 minutes, 2 l. of chloroform was added to the solution, and it was kept at the room temperature over a night. A large amount of crystals (27 g.) separated, but these were found to be unchanged dihydroxystearic acid by their neutr. value and melting point. This experiment was then discontinued.

Thirty-eight grams of dihydroxystearic acid was dissolved in 1.7 l. of alcohol and neutralised with alcoholic potash. Fifty grams of strychnine nitrate (in small excess) was added to the solution, and it was refluxed on the water bath for 1 hour. There was formed a considerable amount of precipitate which seemed to be potassium nitrate. The substances contained in the clear solution separated from the precipitate were subjected to fractional crystallisation, and there were obtained 4 fractions F_1—F_4. The first fraction F_1 was separated further into 8 fractions F_{1-1}—F_{1-8} by means of fractional crystallisation from chloroform. The fraction F_{1-6}, which was most abundant in quantity, was separated further into 5 fractions F_{1-6-1}—F_{1-6-5} from chloroform solution. The fraction F_4 obtained by the first fractional crystallisation was separated into 6 fractions F_{4-1}—F_{4-6} from chloroform solution. Fractions thus obtained were separately examined, but they were found to contain a considerable amount of strychnine and dihydroxystearic acid in free state, and to what extent dihydroxystearic acid was resolved into the optically active isomerides as their strychnine salts was difficult to know.

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(16) The specimen of elaidic acid used for the mixed melting point test was prepared from oleic acid separated from tsubaki oil and had m.p. 43.5–44°.

Summary.

A dihydroxystearic acid, which is contained as a minor component in the fatty acids of castor oil, has been separated and proved to be identical with *d*-9,10-dihydroxystearic acid.

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XII. A FURTHER EXPERIMENT ON THE SEPARATION OF OCTADECATRIENOIC ACID $C_{18}H_{30}O_2$.

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Received August 20th, 1936. Published November 28th, 1936.

In the 1st report[1] of this series the highly unsaturated C_{16}- and C_{18}-acids of sardine oil were examined with the results that hiragonic acid $C_{16}H_{26}O_2$ and moroctic acid $C_{18}H_{28}O_2$ were isolated from C_{16}- and C_{18}-acids, respectively, and the presence of an octadecatrienoic acid $C_{18}H_{30}O_2$ was also indicated. The constitutions of hiragonic and moroctic acids were established in the 2nd and 3rd reports[2] of this series.

The presence of an octadecatrienoic acid in sardine oil was first pointed out by Fahrion.[3] He analysed a fraction of the bromides which was separated from the brominated products of the sardine oil fatty acids as the portion insoluble in petroleum ether, and he believed it to be a hexabromide derived from an octadecatrienoic acid which he named jecoric acid, but there is little doubt that the fraction of the bromides analysed by him is not really a single compound. Although the presence of an octadecatrienoic acid in various kinds of marine animal oils besides sardine oil has been also frequently reported, the evidence for the presence of this acid seems, in most cases, to rest on inadequate experimental results. However, Tsujimoto[4] brought out a strong

(1) This Bulletin, **4** (1929), 83.
(2) This Bulletin, **10** (1935), 192, 232.
(3) *Chem. Ztg.*, **17** (1893), 521.
(4) *Rept Tokyo Imp. Ind. Research Lab.*, **6** (1911), 17; **12** (1917), 169.

evidence for the presence of an octadecatrienoic acid in carp oil and snapping-turtle oil by the finding that the bromine content of ether-insoluble bromides obtained from the fatty acids of these oils lay close to the calculated value for $C_{18}H_{30}O_2Br_6$. In a recent investigation on the oil from *Chanos chanos*, Kafuku and Hata[5] reported the separation of bromides obtained from the liquid fatty acids and found that the fraction which was insoluble in ether but soluble in benzene consisted of a hexabromide which was identical with that derived from linolenic acid. These authors seem to be the first, so far as we know, who indicated the presence of linolenic acid in fish oils with certainty. In the following we describe the results of our further experiments on the separation of octadecatrienoic acid starting with 60 kg. of the ethyl esters of sardine oil fatty acids. In these experiments sufficient indications of the presence of octadecatrienoic acid were obtained, but the separation and the identification of octadecatrienoic acid were not attained. A fraction of octadecatrienoic acid was separated from the debrominated product obtained from the bromides which were insoluble in ether but soluble in benzene, but it could not be freed from the contamination of moroctic and hiragonic acids together with the products of intramolecular polymerisation of these acids. Judging from the results of these experiments, octadecatrienoic acid forms an extremely minor constituent of sardine oil fatty acids.

Experimental.

Sixty kg. of the mixed ethyl esters prepared by the ethanolysis of sardine oil were fractionated, and 28.5 kg. of a fraction boiling below 215°/10 mm. was collected. This fraction was saponified, the fatty acids liberated were dissolved in 85% methanol, and the solution was cooled. The crystalline deposit consisting chiefly of saturated acids was removed by filtration, and the filtrate was neutralised with aqueous solution of lithium hydroxide. The insoluble lithium soaps consisting mainly of the lithium soaps of saturated and mono-ethylenic acids were removed by filtration, and 7.5 kg. of fatty acids were recovered from the filtrate in the usual way. The fatty acids thus obtained were converted into the methyl esters, which were then fractionated yielding 5.9 kg. of a fraction boiling below 215°/15 mm. This fraction was brominated in ethereal solution, and the ether-insoluble bromides were separated and then treated with benzene yielding 1.5 kg. of the bromides soluble in benzene, from which 463 g. of the methyl esters were regenerated by debromination. The methyl esters were fractionated with the following results: (1) below 190°/15 mm. 98 g., (2) 190—205°/15 mm. 175 g., (3) 205—215°/15 mm. 120 g., (4) 215—221°/15 mm. 40 g., (5) residue 30 g. For the details of the above experiments the 2nd report[6] of this series should be consulted, in which the fraction (1) was subjected to a further fractionation for the separation of methyl hiragonate. In the present experi-

(5) *J. Soc. Chem. Ind., Japan*, **38** (1935), 1414.
(6) This Bulletin, **10** (1935), 192.

ment the fraction (3) was fractionated repeatedly, and the following two fractions were collected separately.

Fraction	B.p./15 mm.	Saponif. v.	Iodine v. (Wijs)	Yield (g.)
(a)	205–210°	190.1	291.0	23
(b)	210–215°	190.9	292.4	28

Since the characteristics of the fractions (a) and (b) show no appreciable difference, they were united and subjected to the fractional precipitation of sodium soaps in acetone in the following manner: 45 g. of the fatty acids obtained from the united fractions were dissolved in 360 c.c. of acetone, neutralised with an approximately 4 N alcoholic solution of sodium hydroxide, and alcohol was added until the total volume of the alcoholic solution of sodium hydroxide and the alcohol subsequently added measured 54 c.c. Then 36 c.c. of water and 450 c.c. of acetone were added to the solution, and after heating for a short time the insoluble sodium soaps were precipitated by cooling and filtered. The precipitate and the filtrate were worked up to separate the fatty acids in the usual way.

	Neutr. v.	Iodine v.	Yield (g.)
Fatty acids from the precipitate	201.7	293.8	30.5
Fatty acids from the filtrate	198.6	331.9	14.5

The fatty acids from the precipitate were again fractionated by the sodium-soap-acetone method in the following way: 30 g. of the fatty acids from the precipitate were dissolved in 240 c.c. of acetone, neutralised with an approximately 4 N alcoholic solution of sodium hydroxide, and alcohol was added until the total volume of the 4 N alcoholic sodium hydroxide solution required for neutralisation and the alcohol added measured 30 c.c. Then 30 c.c. of water and 300 c.c. of acetone were added, and after heating for a short time the solution was cooled down to separate the precipitate of insoluble sodium soaps which was filtered and decomposed with hydrochloric acid yielding 23 g. of fatty acids with neutr. value 202.2 and iodine value 284.2. These were fractionated as their methyl esters, (22 g.), and the following fractions were separated.

Fraction	B.p./15 mm.	d_4^{15}	n_D^{15}	Saponif. v.	Iodine v.	Yield (g.)
(1)	199–205°	—	—	—	—	0.4
(2)	205–208°	0.9143	1.4810	197.5	277.4	3.3
(3)	208–212°	0.9144	1.4815	195.4	274.7	4.5
(4)	212–215°	0.9159	1.4825	193.0	267.4	9.9
(5)	215–217°	—	—	—	—	0.6
Residue	—	—	—	—	—	3.3 (diff.)

While the specific gravity and the refractive index, as is seen from the above table, become higher as the boiling point becomes higher, the iodine value falls slightly as the boiling point becomes higher. This is possibly due to a contamination of polymerised methyl esters in the high boiling fractions. The fraction (4) has the characteristics which are close to the calculated values for methyl octadecatrienoate $C_{18}H_{29}O_2CH_3$ (saponif. value 192.0, iodine value 260.6), but it was found from the results of bromination to contain more highly unsaturated methyl esters together with some polymerised methyl esters besides methyl octadecatrienoate. On brominating 7.0 g. of the fraction (4), there were obtained 4.2 g. (60%) of ether-insoluble bromides. These were heated with 400 c.c. of benzene on the water bath under a reflux condenser and then cooled down to about 35°. The insoluble portion was filtered, and on distilling off benzene from the filtrate there remained benzene-soluble bromides with Br-content 65.28% which were higher in Br-content than $C_{18}H_{29}O_2CH_3Br_6$ (62.13% Br). The benzene-soluble bromides were again refluxed with 300 c.c. of benzene, and after cooling the solution to about 30°, a small amount of insoluble bromides was filtered. From the filtrate, 2.5 g. of benzene-soluble bromides were obtained, which had Br-content 64.78% and melted at 195° with slight darkening. The Br-content seems to indicate that the bromides thus obtained contain more highly unsaturated methyl esters besides $C_{18}H_{29}O_2CH_3Br_6$.

Summary.

After having found in a previous study that sardine oil contains an octadecatrienoic acid as a minor constituent of highly unsaturated C_{18}-acids, we have attempted in the present experiment to separate the octadecatrienoic acid starting with a large amount of sardine oil. The results of the present experiment seem to indicate that the octadecatrienoic acid giving an ether-insoluble bromide is contained only in far lesser proportion than presumed before.

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XIII. OXIDATION OF METHYL CLUPANODONATE WITH POTASSIUM PERMANGANATE IN ACETONE SOLUTION.

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Received August 21st, 1936. Published November 28th, 1936.

The constitution of clupanodonic acid, which forms an important constituent of the highly unsaturated acids in sardine oil, was dealt with in the 8th report[1] of this series. Amyl clupanodonate was subjected to ozonolysis, and propionic aldehyde, acetaldehyde, carbon dioxide, succinic acid and amyl hydrogen succinate were identified among the products of ozonolysis. Also the presence of lower acids, which were deemed to consist of propionic and acetic acids, was indicated. Of these compounds propionic aldehyde and propionic acid are derived from the group $CH_3 \cdot CH_2 \cdot CH=$, while acetaldehyde, acetic acid together with carbon dioxide are formed by a further degradation of the products of ozonolysis derived from the group $=CH \cdot CH_2 \cdot CH=$. Succinic acid and amyl hydrogen succinate are evidently derived from the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot COOC_5H_{11}$ respectively. Hence the groups jointed by five ethylenic linkings in clupanodonic acid were found to be $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot COOH$. For the determination of the positions of the respective groups, we made use of the fact that the addition of bromine to the ethylenic linkings in clupanodonic acid proceeds selectively, and prepared dibromo-, tetrabromo- and hexabromo-derivatives of clupanodonic acid by the selective addition of bromine to the ethylenic linkings which lie more distant from the carboxyl group. The products of ozonolysis of these bromo-derivatives were examined, and the following formula of clupanodonic acid was established.

$$CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot COOH.$$

Before our experiment, Inoue and Sahashi[2] oxidised the methyl ester of clupanodonic acid with potassium permanganate in acetone solution, and found

(1) This Bulletin, **10** (1935), 441.
(2) *Proc. Imp. Acad.* (Tokyo), **8** (1932), 371.

butyric, pimelic, succinic, adipic and oxalic acids among the oxidation products. Adipic and oxalic acids were thought by these authors to be formed by the secondary decomposition of pimelic and malonic acids, and consequently the oxidation products primarily derived from the groups jointed by unsaturated linkings in clupanodonic acid were found to be butyric, pimelic, succinic (2 mols), and malonic acids. For the determination of the positions of the respective groups, these authors subjected clupanodonic acid to partial hydrogenation and separated the product into the fractions of different degrees of saturation. The positions of the unsaturated linkings in each fraction were examined by the oxidation with potassium permanganate, and the following formula having one triple linking and three double linkings was proposed for clupanodonic acid.

$$CH_3\cdot(CH_2)_2\cdot C\equiv C\cdot(CH_2)_5\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

While we used the ozonide method for the determination of the constitution of clupanodonic acid, Inoue and Sahashi used the permanganate method for the same purpose, but the difference of the oxidation method can not explain well the marked discrepancies between the results of our previous experiment and those obtained by Inoue and Sahashi. Leaving the positions of the respective groups jointed by unsaturated linkings undiscussed, it can hardly be accepted that the oxidation products obtained in our experiment on the amyl ester of clupanodonic acid by the ozonide method and those obtained by Inoue and Sahashi from the methyl ester of clupanodonic acid by the permanganate method resulted from the same single compound. It should, however, be noted that while the specimen of clupanodonic acid used for the determination of the constitution in our experiment was freed from C_{22}-acids of different degrees of unsaturation as far as possible and possessed high purity, the purities of specimens of clupanodonic acid which had been separated by several authors before our experiment are doubtful from the contamination of acids of different degrees of unsaturation. But such difference in the purity of clupanodonic acid alone can not explain the discrepancies between the results of our experiment and those obtained by Inoue and Sahashi. The following descriptions are the results of our experiment on the oxidation of methyl clupanodonate with potassium permanganate in acetone solution.

Among the products of oxidation of methyl clupanodonate with potassium permanganate in acetone solution, propionic acid, acetic acid, succinic acid and methyl hydrogen succinate were identified. Acetic acid is believed to be

formed by the secondary decomposition of malonic acid, and consequently the groups jointed by ethylenic linkings in clupanodonic acid were found to be $CH_3{\cdot}CH_2{\cdot}CH=$, $=CH{\cdot}(CH_2)_2{\cdot}CH=$, $=CH{\cdot}CH_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}COOH$, of which three of the group $=CH{\cdot}(CH_2)_2{\cdot}CH=$ are present since clupanodonic acid has 22 carbon atoms in total. These results agree fully with those obtained by the ozonolysis of amyl clupanodonate in the previous experiment. Whilst the finding of the group $CH_3{\cdot}(CH_2)_2{\cdot}CH=$ by Inoue and Sahashi at the terminal opposite to the carboxyl group is based on the detection of butyric acid among the oxidation products, we could not find butyric acid, but we separated propionic acid which was identified as its *p*-bromophenacyl ester in pure state. Neither adipic acid nor pimelic acid could be found among the oxidation products in our experiment. In short, the oxidation products obtained in our experiment on methyl clupanodonate by means of potassium permanganate differ from those reported by Inoue and Sahashi, and the results of our experiment agree fully with those of the previous experiment of the ozonolysis of amyl clupanodonate. It is quite certain that clupanodonic acid has no triple linking but it has five ethylenic linkings. The structure is $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$-docosapentenoic acid as has been established by the previous experiment.

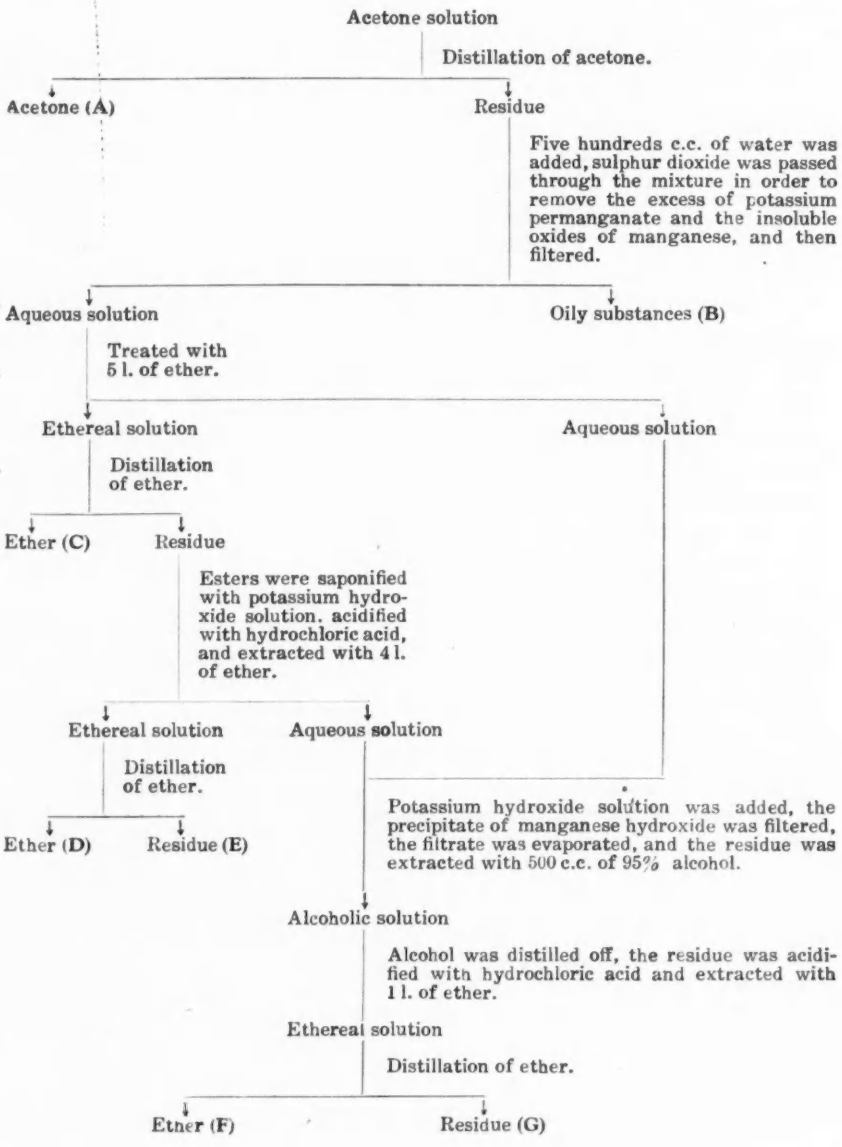
Experimental.

1. **Oxidation of Methyl Clupanodonate and Separation of Oxidation Products.** Methyl clupanodonate used in the present experiment was the same as described in the 7th report[3] of this series, and had d_4^{15} 0.9240, n_D^{15} 1.4955, saponif. value 163.0 (calc. 163.0) and iodine value (Wijs) 368.0 (calc. 368.6). Amyl clupanodonate and free clupanodonic acid used for the experiment of ozonolysis described in the 8th report[4] of this series were prepared from the same specimen of methyl clupanodonate.

Ten grams of methyl clupanodonate was dissolved in 200 c.c. of acetone, and 150 g. of potassium permanganate was added in small portions. In order to avoid a violent heat evolution, the solution was cooled at first and then potassium permanganate was added. After the heat evolution has ceased, the solution was heated on the water bath under a reflux condenser. Before the addition of a further quantity of potassium permanganate the solution was cooled, and then potassium permanganate was added. After the heat evolution has ceased, the solution was again heated. Repeating these operations the entire quantity of potassium permanganate was added in the course of 5 hours. The solution was refluxed for 5 hours more, and then the oxidation products were separated into several fractions as shown in Table 1.

(3) This Bulletin, **10** (1935), 433.
(4) This Bulletin, **10** (1935), 441.

Table 1.


Acetone solution
Distillation of acetone.
Acetone (A)
Residue
Five hundreds c.c. of water was added, sulphur dioxide was passed through the mixture in order to remove the excess of potassium permanganate and the insoluble oxides of manganese, and then filtered.
Aqueous solution
Oily substances (B)
Treated with 5 l. of ether.
Ethereal solution
Aqueous solution
Distillation of ether.
Ether (C)
Residue
Esters were saponified with potassium hydroxide solution. acidified with hydrochloric acid, and extracted with 4 l. of ether.
Ethereal solution
Aqueous solution
Distillation of ether.
Ether (D)
Residue (E)
Potassium hydroxide solution was added, the precipitate of manganese hydroxide was filtered, the filtrate was evaporated, and the residue was extracted with 500 c.c. of 95% alcohol.
Alcoholic solution
Alcohol was distilled off, the residue was acidified with hydrochloric acid and extracted with 1 l. of ether.
Ethereal solution
Distillation of ether.
Ether (F)
Residue (G)

2. **Oxidation Products Distilled off with the Solvents.** The acetone (A) and the ether (C, D, F), which were recovered in the separative operations shown in Table 1, showed acidic reaction. The acetone (A) was neutralised with potassium hydroxide, acetone was distilled off, and there remained the potassium salts. The ether (C, D, F) was shaken with potassium hydroxide solution by which the acidic substances were converted into the potassium salts and separated from the ethereal solution. The aqueous solution of potassium salts was evaporated to dryness and there remained the potassium salts as residue. The potassium salts thus obtained were united and treated with warm 95% alcohol in which potassium sulphite remained insoluble. The alcoholic solution was separated and evaporated. The residue was acidulated with dilute sulphuric acid and distilled. The distillate still contained sulphur dioxide. For the removal of last traces of sulphur dioxide, potassium permanganate was added to the distillate, and the solution was redistilled. The yield of final distillate was 43 g., and it had acid value 9.6, from which the total amount of acids contained in the distillate was calculated to be 0.44 g. as acetic acid. Thirty grams of distillate was nearly neutralised with N/10 alcoholic potash, and after addition of 1.4 g. of *p*-bromophenacyl bromide the solution was refluxed for 2 hours. A large amount of water was then added, and the separated solid was recrystallised from 60% alcohol. The crystals obtained melted at 84.5–85° both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of acetic acid.

3. **Oxidation Products Dissolved in Water.** The residues (E) and (G) in Table 1 consisted of a mixture of crystalline solid and liquid. These were united and treated with petroleum ether (b. p. below 50°). The petroleum ether solution and the insoluble portion were separated.

(i) *Petroleum ether solution.* The solution was first heated on the water bath until the bulk of petroleum ether distilled over. It was then heated in an oil bath, and the distillate, which distilled over below 100° and was contaminated with a large proportion of petroleum ether, was collected and united with petroleum ether obtained before. The yield of distillate thus obtained was 154 g. It had acid value 4.3, from which the acidic substances contained in the distillate were calculated to be 0.71 g. as acetic acid. The *p*-bromophenacyl ester was prepared from the acidic substances contained in the distillate, and it was recrystallised from 60% alcohol yielding crystals which melted at 82–83° and showed no depression of melting point when admixed with a pure specimen of *p*-bromophenacyl ester of acetic acid (m. p. 84.5°) in various proportions. The portion which did not distil below 100° amounted to 1.9 g. It yielded two fractions on further heating: (1) b.p. 100–130°, 0.25 g.; (2) b. p. 130–140°, 0.8 g. Above 140° practically no distillate was obtained, and when the temperature of the oil bath reached 200° the residue began to show the indications of decomposition. The fraction (1) consisted mainly of propionic acid, and had n_D^{20} 1.3871 and neutr. value 763.2 (calc. 757.7). The *p*-bromophenacyl ester, when recrystallised from 70% alcohol, melted at 62.5–63° both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of propionic acid. The final residue from distillation was a dark brownish viscous oil which was considered to be intermediate products which escaped a complete oxidation. It was subjected to a further oxidation by means of an alkaline solution of potassium permanganate, and the products were acidified and taken up with ether. On removal of ether from ethereal solution, there remained a crystalline solid (0.1 g.) which appeared to be impure succinic acid from its melting point 178–179°.

(ii) *The portion insoluble in petroleum ether.* This portion (7.5 g.) consisted of a mixture of reddish orange liquid and crystalline solid. It was washed with cold ether for

the removal of liquid portion, and the crystalline solid (a) was separated. The liquid portion obtained from the ethereal washing appeared to contain the substances which escaped a complete oxidation. It was subjected to a further oxidation with an alkaline solution of potassium permanganate. After acidification the products were taken up with ether, and on removal of ether there was obtained crystalline solid (b) which was still contaminated with a small proportion of oily substances. The crystalline solids (a) and (b) were united and recrystallised from ethyl acetate, yielding 1st crop of neutr. value 950.1 and m.p. 181-182° and 2nd crop of neutr. value 950.0 and m.p. 180-181°. Each crop showed no depression of melting point when admixed with a pure specimen of succinic acid (neutr. value calc. 950.6, m.p. 182-183°).

4. **Oily Substances.** Yield 3.6 g. These substances (B) contained some neutral substances which escaped oxidation. For the separation of acidic substances, the mixture was dissolved in ether and shaken with potassium hydroxide solution. The acidic substances were converted into the potassium salts and separated from ethereal solution. After the acidification of the aqueous solution of potassium salts with hydrochloric acid, the acidic substances liberated were taken up with ether. On distillation of ether, there were obtained 1.9 g. of acidic substances which showed neutr. value 432.1 and saponif. value 835.1 which are close to the calculated values for methyl hydrogen succinate (neutr. value 424.8, saponif. value 849.7). The free acid prepared from this acid ester by saponification followed by acidification melted at 179-180° after being washed with a little cold ether. The melting point was not lowered when the substance was admixed with succinic acid in various proportions.

Summary.

Methyl clupanodonate has been oxidised with potassium permanganate in acetone solution. Among the oxidation products propionic acid, acetic acid, succinic acid and methyl hydrogen succinate have been identified. Of these compounds acetic acid is believed to be formed by the secondary decomposition of malonic acid. Accordingly the presence of above-mentioned oxidation products gives an indication of the presence of the following groups in clupanodonic acid jointed by ethylenic linkings thus: $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$. These results agree fully with those obtained in a previous experiment of the ozonolysis of amyl clupanodonate.

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THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XIV. OXIDATION OF POTASSIUM CLUPANODONATE WITH POTASSIUM PERMANGANATE IN AQUEOUS SOLUTION.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received September 4th, 1936. Published November 28th, 1936.

As described in the preceding report[1] of this series, the oxidation of methyl clupanodonate with potassium permanganate in acetone solution yielded propionic acid, acetic acid, succinic acid and methyl hydrogen succinate. Since acetic acid is believed to be formed by the secondary decomposition of malonic acid, the above results indicated that the respective groups jointed by the ethylenic linkings in clupanodonic acid consisted of $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$, and they agreed fully with the results derived from the ozonolysis of amyl clupanodonate in the 8th report[2] of this series. The present paper deals with the results of the oxidation of potassium clupanodonate with potassium permanganate in aqueous solution. In the present experiment propionic acid, acetic acid and succinic acid were separated and identified from the oxidation products, and also the presence of malonic acid was indicated. Of these compounds acetic acid is considered to be formed by a further degradation of malonic acid which was formed primarily from the group $=CH \cdot CH_2 \cdot CH=$. Accordingly the respective groups jointed by the ethylenic linkings in clupanodonic acid consist of $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$ assuming that the terminal group containing carboxyl group is $=CH \cdot (CH_2)_2 \cdot COOH$. These results also agree fully with those derived from the ozonolysis of amyl clupanodonate and the permanganate oxidation of methyl clupanodonate in acetone.

Experimental.

1. Oxidation of Potassium Clupanodonate with Potassium Permanganate in Alkaline Aqueous Solution. Clupanodonic acid used in the present experiment is the same as that used in the previous experiment of ozonolysis, and had the following characteristics: d_4^{15} 0.9390, n_D^{15} 1.5035, neutr. value 170.4 (calc. 169.8), iodine value (Wijs) 383.2 (calc. 384.2).

(1) This Bulletin, **11** (1936), 745.
(2) This Bulletin, **10** (1935), 441.

Five grams of clupanodonic acid was mixed with 2 g. of potassium hydroxide and 500 c.c. of water giving a dilute alkaline solution of potassium clupanodonate. The solution was ice-cooled, and solutions of potassium permanganate were added gradually with constant stirring. Solutions of potassium permanganate consisted of 500 c.c. of a 2% solution, 400 c.c. of a 3% solution, 450 c.c. of a 4% solution and 400 c.c. of a 5% solution which were added successively in the course of 3 hours. After addition of the entire quantity of potassium permanganate, the solution was allowed to stand in an ice box for 17 hours, and then sulphur dioxide was passed through the solution in order to reduce the excess of potassium permanganate. The solution was then filtered with suction, and the precipitate of brown oxides of manganese was washed several times with hot water, using 300 c.c. each time. The filtrate and the washings were united, and after making the solution slightly alkaline, it was evaporated to dryness, and then acidulated with dilute sulphuric acid. The total volume of the solution was made up to about 100 c.c., and it was extracted with 5 l. of ether. The ether (a) was removed from ethereal solution by distillation, and there was obtained 7.3 g. of residue which was then extracted three times with petroleum ether using 100 c.c. each time. The petroleum ether solution and the insoluble portion (b) were separated. On distilling the petroleum ether solution, the distillate (c) boiling below 100° which consisted mainly of petroleum ether containing only a small proportion of other volatile substances was separated, and there remained 1.1 g. of residue (d).

2. **Oxidation Products Carried over with Solvents.** The ether (a) and the distillate (c) consisting largely of petroleum ether showed acidic reaction. These were shaken with potassium hydroxide solution, and the acidic substances were separated as the potassium salt solution. On acidification with sulphuric acid, the acidic substances were liberated, and after addition of a small amount of potassium permanganate, which oxidised sulphurous acid dissolved in the solution, it was distilled. The distillate amounted to 29 g. and had acid value 12.2, from which the acidic substances contained in the distillate is calculated to be 0.38 g. as acetic acid. The distillate was neutralised with alcoholic potash and refluxed with calculated amount of *p*-bromophenacyl bromide. The *p*-bromophenacyl ester formed was separated and recrystallised from 60% alcohol, giving crystals which melted at 84.5–85°, both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of acetic acid.

3. **The Portion Soluble in Petroleum Ether.** The residue (d) obtained by removing the solvent from petroleum ether solution formed an orange yellow liquid. On distilling this portion the following two fractions were separated: (1) below 130°, 0.11 g.; (2) 130–140°, 0.22 g. The fraction (2) was converted into the *p*-bromophenacyl ester which on recrystallisation from 70% alcohol melted at 61.5–62°. The melting point was not lowered when the substance was admixed with *p*-bromophenacyl ester of propionic acid, m.p. 62.5–63°, in various proportions. The final residue from distillation was a dark brownish viscous liquid and appeared to contain intermediate oxidation products which escaped a complete oxidation. It was subjected to a further oxidation with an alkaline solution of potassium permanganate, and after acidification the product was taken up with ether. Removal of ether from ethereal solution left behind a mixture of crystalline solid and viscous liquid. The latter was removed by washing with a little cold ether, and there was obtained a crystalline solid which consisted of impure succinic acid melting at 178–179°.

4. **The Portion Insoluble in Petroleum Ether.** This portion (b) amounted to 5.8 g. It was washed with cold ether, and there remained 2.9 g. of crystalline solid (i). On removal of ether from the ethereal washing there remained a reddish orange liquid which was contaminated with a small proportion of crystalline solid and contained possibly substances of relatively high molecular weight which escaped a complete oxidation. For a further oxidation, it was oxidised by using 130 c.c. of an alkaline solution (5%) of potassium permanganate, and after treatment with sulphur dioxide, the product was taken up with ether. On removal of ether from ethereal solution there was obtained 2.6 g. of crystalline solid (ii) which was still contaminated with a small proportion of liquid substances. The crystalline solids (i) and (ii) were united and recrystallised from ethyl acetate, yielding succinic acid of neutr. value 950.1 (calc. 950.6) and m.p. 180–181°. On removal of ethyl acetate from the mother liquor from recrystallisation there remained a mixture of crystalline solid and viscous liquid, which was then extracted with a little water in which viscous liquid remained insoluble. The aqueous extract was saturated with sodium chloride and shaken with a large amount of ether. A crystalline substance was obtained after removal of ether from the ethereal solution. It had neutr. value 988.4 and decomposed when heated at 135°. On passing the volatile substances formed by the decomposition into a solution of barium hydroxide, it became turbid.

Summary.

Potassium clupanodonate has been oxidised with potassium permanganate in alkaline solution under cooling. Among the oxidation products, propionic, acetic and succinic acids have been separated. Also the presence of malonic acid is indicated. Of these compounds acetic acid is believed to be formed by a further degradation of malonic acid, and consequently the above results show that the respective groups jointed by the ethylenic linkings in clupanodonic acid are $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$, provided the terminal group containing the carboxyl group is assumed to be $=CH \cdot (CH_2)_2 \cdot COOH$. The results of the present experiment agree fully with those obtained in the previous experiments of the ozonolysis of amyl clupanodonate and the permanganate oxidation of methyl clupanodonate in acetone solution.

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THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF VARIOUS SUBSTANCES. II. FURTHER EXPERIMENTS ON THE EFFECTS OF FERRO-MAGNETIC CATALYSTS.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

Received November 2nd, 1936. Published November 28th, 1936.

In the absence of oxygen and peroxides or in the presence of an anti-oxidant such as diphenylamine hydrogen bromide adds slowly to allyl bromide and the product consists mainly of 1,2-dibromopropane (the normal addition), while in the presence of oxygen or a peroxide such as benzoyl peroxide the addition is rapid and 1,3-dibromopropane is mainly produced (the abnormal addition).[1] As reported in the previous paper[2] the authors found that the ferro-magnetic metals, iron and nickel, exert an influence similar to that of oxygen and peroxides on the addition of hydrogen bromide to allyl bromide, accelerating the abnormal addition. The experiments recorded in this paper have been carried out further to investigate the effects of ferro-magnetic substances on the addition of hydrogen bromide to allyl bromide. The experimental procedure and the conditions of addition were all the same as in the experiments recorded in the previous paper. The catalysts were heated at 250° in vacuum for an hour and then washed with pure hydrogen bromide gas. Each addition was carried out with 24 g. or 0.2 mol of allyl bromide and 20 g. or 0.25 mol of hydrogen bromide. The accompanying table shows the results of additions in the dark at room temperature in the absence of solvents and air, reaction time being three days.

Although, in the previous experiments on the effects of iron and nickel, peroxide-free allyl bromide was used and air was excluded; experiments were repeated with the addition of diphenylamine (0.5 g.), other conditions being unaltered. As shown in the table (experiments 1,2, and 4), the results are quite similar to those obtained without the antioxidant (compare the table in the previous paper). Therefore, the effect observed in the experiments with the ferro-magnetic metals can be undoubtedly attributed to the metals, and the possibility of the participation of oxygen or peroxides which might have been present by any chance can be excluded.

(1) M.S. Kharasch and F.R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.
(2) This Bulletin, **11** (1936), 692.

No. of exp.	Catalyst and amount added (g.)	Products				Remarks
		Yield (%)	Boiling point (°C./mm.)	Dibromopropanes (%)		
				1,3-	1,2-	
1	Reduced iron 3.4	39	53–65/22	78	22	Diphenylamine 0.5 g. Shaken
2	,, ,,	33	48–62/18	71	29	Diphenylamine 0.5 g.
3	,, ,,	35	50–65/22	68	32	Magnetic field (5700 gausses) applied
4	Reduced nickel 3.5	32	45–58/16	58	42	Diphenylamine 0.5 g. Shaken
5	,, ,,	37	45–54/23	17	83	Nickel placed in air for 5 weeks after preparation Shaken
6	Reduced cobalt 3.5	42	38–43/16	7	93	Commercial cobalt Diphenylamine 0.5 g. Shaken
7	,, ,,	40	37–50/15	30	70	Freshly reduced cobalt Diphenylamine 0.5 g. Shaken
8	Iron-sand 4.6	47	45–48/24	12	88	Shaken
9	,, ,,	44	45–48/23	7	93	

All the additions recorded in the present and the previous papers took place in Pyrex glass tubes placed in a bomb-furnace or in an iron pipe, except experiment 3, where the Pyrex tube was placed in a magnetic field of about 5700 gausses, although the intensity of the field was far too small to expect any effect. The results are well within the range of the results obtained without the magnetic field.

If iron and nickel act as surface catalysts in the addition of hydrogen bromide to allyl bromide, their action must be governed by the conditions of the surface. In experiment 5, reduced nickel, which had been placed in air for five weeks after preparation and had taken a brown colour, was used. In this case, the effect of the metallic nickel on the direction of addition was far repressed. The good yield of the addition products may be attributed to the action of nickel oxide or bromide. In all other experiments with nickel the freshly reduced metal was used. In experiments with iron, the commercial reduced iron (Kahlbaum) was employed throughout. Thus it cannot be certain that the surface was clean from the oxide of iron. The oxide of iron would react with hydrogen bromide yielding ferric bromide. Ferric

chloride is known by Kharasch and Mayo to possess a tremendous accelerating effect upon the normal addition[3]. Therefore, if freshly reduced iron is used, effect of the metal may appear more conspicuous.

Cobalt was attacked by hydrogen bromide to a great extent, and a green solid substance was formed in the reaction mixtures, covering the metal. On this account, with commercial reduced cobalt (Kahlbaum) no effect (experiment 6), and even with freshly reduced cobalt but a slight effect (experiment 7), on the direction of addition were observed. The remarkable increasing effect on the yields of the products may be attributed to the action of the cobalt salt.

With a view to testing a strongly magnetic compound, iron-sand was used (experiments 8 and 9). The formation of a considerable amount of ferric bromide was shown by the intense brown colour of the reaction mixtures, and in accordance with it the yields of the reaction products were extremely increased without any marked influence on the composition of the products.

Further the authors have obtained some interesting results in the experiments with platinum black and oxygen or peroxides. The details will follow.

The authors express their hearty thanks to the Imperial Academy of Japan for a grant.

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(3) *Loc. cit.* see p. 2489.

THE FORMATION OF AN ISOMERIDE OF NEOERGOSTEROL BY THE PYROLYSIS OF ERGOPINACONE.

By Yoshiyuki URUSHIBARA and Toshio ANDO.

Received October 30th, 1936. Published November 28th, 1936.

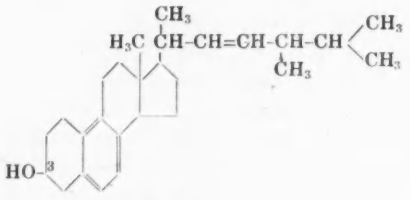
Ergopinacone (14 g.) prepared from ergosterol (24 g.) according to the directions of H. H. Inhoffen[1] was subjected in portions of 1 g. to decomposition at 190° under the pressure of 0.15–0.25 mm. followed by the immediate distillation at 210–250° under 0.001–0.01 mm. Crystallization of the distillate from ethanol by adding water yielded crude neoergosterol (5.8 g.) melting at 129–134° (corr.). The crude neoergosterol (3 g.) was acetylated with acetic anhydride and the product was fractionally recrystallized from acetone. From the less soluble part pure neoergosteryl acetate (0.66 g.) was obtained in needles melting at 123.5–124° (corr.) (Found: C, 82.49, 81.90; H, 10.41, 10.36. Calculated for $C_{29}H_{42}O_2$: C, 82.41; H, 10.02%). Windaus[2] and Inhoffen[1] give melting point 122–123°. From the more soluble part another substance (0.7 g.) forming fine prisms melting at 108–109° (corr.) was obtained. It gave the same analytical results as neoergosteryl acetate (Found: C, 82.33, 82.24; H, 9.96, 10.35. Calculated for $C_{29}H_{42}O_2$: C, 82.41; H, 10.02%). Its melting point did not rise on further recrystallization. The mixtures of this substance with neoergosteryl acetate melted at 105–108° (corr.) and at 106–115° (corr.) according as the portion of the latter was smaller and greater. Thus it was shown that the new substance is the acetate of an isomeride of neoergosterol, which the authors call "iso-neoergosterol." Hydrolysis of the acetate (100 mg.) melting at 108–109° with alcoholic potash and recrystallization of the product from methanol gave free iso-neoergosterol (58 mg.) in prisms melting at 138–139° (corr.) (Found: C, 84.63, 84.43; H, 10.47, 10.87. Calculated for $C_{27}H_{40}O$: C, 85.19; H, 10.60%).

The crude neoergosterol (1 g.) was then recrystallized from ethanol. From the less soluble part pure neoergosterol (0.4 g.) was obtained, melting point 152–153° (corr.) (Found: C, 84.59, 84.65; H, 10.84, 11.06. Calculated for $C_{27}H_{40}O$: C, 85.19; H, 10.60%). Windaus and Inhoffen give melting point 151–152° (corr.). By the recrystallization of the more soluble part from methanol iso-neoergosterol (0.4) was obtained in prisms melting at 138–139°

(1) *Ann.*, **497** (1932), 130.
(2) Windaus and Borgeaud, *Ann.*, **460** (1928), 235.

(corr.) alone or in admixture with the specimen from the acetate (Found: C, 84.47; H, 10.99. Calculated for $C_{27}H_{40}O$: C, 85.19; H, 10.60%).

If iso-neoergosterol is demonstrated as the stereoisomeride of neoergosterol with regard to the carbon atom 3, it may be concluded that the carbon atom 3 takes part in the formation and the pyrolytic decomposition of ergopinacone and some light will be thrown on the yet unexplained chemical structure of the dimolecular derivative of ergosterol.



Neoergosterol

The authors express their hearty thanks to Mr. Yasohachi Yamaguchi of Teikokusha Co. for his generous support of this work.

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